# NITROSYL COMPLEXES OF MONOVALENT CHROMIUM

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# CERTIFICATE

This is to certify that the work embodied in the thesis entitled, "MITROSYL COMPLEXES OF MONOVALENT CHROMIUM" has been carried out by Sri Ram Charitra Maurya, Department of Chemistry, Atarra F.G.College, Atarra(Banda) under my supervision. He has full filled the requirements for the degree of Doctor of Philosphy in Chemistry of the Bundelkhand University, Jhansi regarding the nature and prescribed period of investigational work. The work reported in this thesis embodies the work of candidate himself.

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Dedicated to my revered father,

Shri Purusottam Maurya,

who has always been

a source of

inspiration

to me.

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### PREFACE

The investigation on the chemistry of chromium embodied in this thesis has been carried out in the Inorganic Chemistry Laboratories, T.D.College, Jaunpur and in Chemical Laboratories Atarra Post Graduate College, Atarra (BANDA).

The inception of nitrosyl Chemistry starts with the isolation of nitroprusside in 1849. But the knowledge of nitrosyl chemistry of chromium in monovalent oxidation state is very meagre uptil now and the present study involves the chemistry of nitrosyl complexes of chromium in this oxidation state. New series of complex compounds of monovalent chromium have been prepared and described in this thesis including penta-and hexacoordinated nonelectrolyte species using cyanide, thiocyanate, diethyldithiocarbamate, acetylacetone and a few mono and bidentate ligands, some of which are quite novel containing cyano bridging. Structural aspects of some of the representative type of complexes have been undertaken with the help of magnetic, infrared, electronic, electron spin resonance, x-ray photoelectron and mass spectral studies.

The reference cited in this thesis are covered upto the year 1978 and the part of the work presented in this thesis has been published in some Journals of Chemistry.

I wish to express my deep sense of gratitude to Professor R.P.Rastogi, Fh.D., F.N.A., Head of the Department of Chemistry, Gorakhpur University and Dr.S.Sarkar, Lecturer in Chemistry Department, I.I.T., Kanpur for suggesting the

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Jan., 1981.

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# GLOSSARY OF SYMBOLS

		FF033WLL OL 3111DAFA
AG	s & 4	Angstrom Unit, 10 <sup>-8</sup> cm
acac	4 m 6	actylecetonate
diars	***	o-phenylenebisdimethylersine
dipy	* * *	2,2° dipyridyl
DTC	(b) (b) (a)	diethyldithiocarbamate
SN	* * *	ethylenediam <b>ine</b>
		ethyl
e.S.T.	* * *	electron spin resonance
e\	4 4 4	electron volt
I.R.	* * *	Infrared
	* * *	ligend
ñ <b>e</b>	* * *	methyl
RD	5	Molecular orbital
NCS	* * *	thicyanate
o-phen	***	ortho-phenenthroline
Ph		henyl
ру		pyzidine
FPha	n 40 m	triphenyl phosphine
Qu	* * *	quincline
XPS		X-ray photoelectron spectroscopy
)		stretching frequency, cm -1
m		nanometer, 10 <sup>-9</sup> m = 10A°
8	<b>0 0 0</b>	bending frequency, cm 1
E	* * *	molar extinction coefficient

// ... effective magnetic moment in B.M.

// ... magnetic susceptibility

// beta
// gama

// molar conductance

# Chapter I

This chapter describes a brief and general account of the cyanonitrosyl complexes of transition metals followed by their bonding nature and structural aspects. As an out come of these, the scope of the present work has also been stressed in this chapter.

# A-INTRODUCTION

Transition metal complexes containing nitric oxide as a coordinating ligand have been known by for over a century. In this field, experiment has, in the main, out run theory. This is so because NO is treated as a good ligand comparable to CO, yet the main differences between these two ligands are:

- (1) a wide variety of reagents can be employed as a source for nitrosylation whereas in carbonyl complexes, it is dominated by using CO as the source for carbonylation in varied temperatures and pressures.
- (2) The apparent lack of reactivity of nitrosyl complexes compared to the carbonyl complexes. The development of new approaches in synthesizing nitrosyl complexes stemmed from the usefulness of nitrosylation using NO with high pressure high temperature technique due to its thermodynamic instability and its tendency to function as an oxidising agent.

3 NO --> 
$$N_2$$
0 + NO<sub>2</sub> H = -37.2 kcal mol<sup>-1</sup> .. (1)

$$NO \longrightarrow \frac{1}{2}N_2 + \frac{1}{2}O_2$$
  $H = -21.6 \text{ kcal mol}^{-1}$  .. (2)

The mode of bonding of coordinated NO and CO have long been considered as analogous and in that sense CO, CN $^-$ , NO $^+$  and N $_2$  as isoelectronic ligand, coordinate in a similar manner because they have same external electronic configuration. The bonding in nitrosyl complexes in the

simplest form is assumed as an electron transfer from NO to the metal proceeds the coordination of NO+ through the nitrogen lone pair. A -back donation from the metal to the \* antibonding orbital of the NO reinforces the lone electron pair donation of nitrogen. In this sense NO functions as a three electrons donor compare to other isoelectronic ligands which are formally two electrons donor, 2-4 In this type of mode of bonding several attempts were made to interpret the wide region of 1950-1100 cm<sup>-1</sup> nitrosyls stretching in infrared spectral studies. To cover the lowest range of ) (NO) for the red isomer of [Co(NH3)5NO] 2+, it was argued that there was a transfer of an electron from the metal to NO, the NO then acting as a normal ligand with donation of two electrons to the metal 5. However, the red isomer of [Co(NH<sub>q</sub>) = NO] 2+ was latter found to have a quite different structure which is a dimeric cation  $\{[Co(NH_3)_5]_2(N_2O_2)\}^{4+}$ , where the hyponitrite ion is asymmetrically bonded to the two cobalt moiety in a trans arrangement.

The long search for NO $^-$  complex predicted as early as 1934 by Sidgwick $^{1(a)}$  culminated in the complex  $[Ir(C1)(C0)(N0)(PPh_3)_2]$   $BF_4$ . In this case  $NO^+$  is believed to be coordinated as a Lewis acid accepting an electron pair from the weak base iridium(I). In other

words the coordinated nitrosyl group can be treated as NO in the formal oxidation state of iridium as +3. In other words two canonical forms may be depicted as follows:

Thus it is generally assumed that in the bent form of coordinated NO, it functions as a one electron donor.

Besides these two extreme formulations of terminal bonding of nitrosyl group, in a few cases it can acts as a doubly bridging group, for example  $(h^5-C_5H_5)(NO)Cr(\mu-NO)(\mu-NH_2)Cr(NO)(h^5-C_5H_5)^7$ . No can acts even as triply bridging group as has been observed in the complex  $(h^5-C_5H_5)_3\text{Mn}_3(NO)_4\text{B}$ .

Cyanonitrosyl complexes have drawn a distinction from other metal nitrosyls, although they are not basically different from other nitrosyl complexes. Among these  $\left[ \Pi(\text{CN})_{\text{S}} \text{NO} \right]^{\text{n-}}$  species have received special attention. A survey on the existing literatures suggest the formation of these species from different transition metals as shown in Table -1.

# Table-1

٧	Cr	Πn	Fe
X	Mo	X	Ru
х	Х	Re	0s

In other stereochemistry, nickel forms[NiNO(CN)<sub>3</sub>]<sup>2-</sup> as tetrahedral geometry<sup>9</sup> and vanadium gives, K<sub>4</sub>[VNO(CN)<sub>6</sub>] as pentagonal bipyramidal geometry.10,11

The cyanonitrosyl complexes were synthesized using typically different methods. Each method is suitable for a particular transition metal as summarised below:

# (i) The action of nitric acid on a cyano complex of a transition metal:

This method has been first employed for the preparation of sodium pentacyanonitrosylferrate, commonly called sodium nitroprusside by the reaction of nitric acid on sodium hexacyanoferrate. 12 The same method has been used for the preparation of analogous ruthenium and osmium complexes. 13 Treatment of  $Na_3[Re(CN)_5(H_2^0)]$  with moderately strong nitric acid is said to yield  $Na_2[Re(CN)_5N0]$  14. A diamagnetic nitrosylcyano complex of suggested composition  $Ag_3[Re(CN)_7(N0)]$ , obtained (contaminated with AgCN), when  $K_3[Re(CN)_8]$  is warmed with 2 molar nitric acid. 15

# (ii) The reaction of nitric oxide on a cyano complex of

# A a transition metal:

Nitric oxide reacts with  $K_4[Ni_2(CN)_6]$  in liquid ammonia suspension to form deep violet  $K_2[Ni(CN)_3(NO)]$ . <sup>16</sup>
(iii) Alkaline hydroxylamine method:

Hieber and coworkers first exploited the use of hydroxylaminehydrogenchloride as a nitrosylating agent 17 tracing back an observation made by Vonder Heid and Hofmann. 18 The reaction of MoDa, KOH and hydroxylaminehydrogenchloride in aqueous medium gives a violet product of composition, K4[Mo(NO) (CN)5].2H,0.17 There was some controversy to formulate this compound and an alternate octacoordinated structure K4 [No(OH)2(CN)5] was proposed by Griffith, Lewis and Wilkinson. 19 X-ray studies finally confirm the hexacoordinated structure and composition of the compound is really  $K_4[Mo(NO)(CN)_5]$ .  $2H_2O$ .  $^{2O}$ Wilkinson and coworkers then utilized this procedure on other exemetallate anions. Thus with CrO 2-, the green complex K3[CrNO(CN)5]. H20 was isolated. 19 Similarly using the same procedure with VO, an orange coloured complex of composition,  $K_5[VN0(CN)_5]$ .  $2H_2^0$  was isolated 21which was structurally characterized as Ka[VNO(CN), 2H,0 by X-ray crystallography. 22 Interestingly using a slight different procedure that is a VO3 and hydroxylamine method, passes of HoS leads to the isolation of yellow

coloured complex K<sub>4</sub>[VNO(CN)<sub>6</sub>]. <sup>10</sup>H<sub>2</sub>O. It is interesting to know that for other exemetallates this method remains unsuccessful.

# (iv) Preparation using redox reactions:

It is noteworthy to mention that the use of nitric acid as nitrosylating agent has been successfully applied to the synthesis of nitroprusside and its ruthenium and osmium analoges in the same formal oxidation states. Though oxidation state of the central metal attached with NO has got no sense in the real sense of the term. yet a formalism containing (MNO) n+ would avoid an extreme formalism of NO mither as NO or NO (vide infra). this sense by following the same process of preparation, Fe, Ru and Os give (MNO) 3+ moiety in their complexes. Contrary to this using hydroxylamine method of preparation chromium gives (CrNO) 2+ group whereas molybdenum gives (MoNU) + moiety. This prompted Griffith 23 to reduce the (CrNO) 2+ group containing compound, Ka[CrNO(CN)].H20 using polarographic method of reduction to isolate a blue reduced species KA [CrNO(CN) ] . H20 analogous to KA [MoNO(CN) ] There has been several attempts to isolate the one electron oxidation product of Ka[MoNO(CN)] to obtain[MoNO(CN)] 3anion analogous to [CrNO(CN) ] 3-, 24,25 but the pure green product, (PPh4)3[MoNU(CN)5].2H20 was isolated only very recently using air as oxidising agent. 26 Similarly

the purple coloured complex  $K_3[MnNO(CN)_5]$ .  $2H_2^0$  on oxidation with bromine or nitric acid gives yellow  $K_2[MnNO(CN)_5]$ .  $2H_2^0$ . The reduction of sodium nitroprusside with sodium in liquid ammonia yields ochrevellow compound  $Na_3[FeNO(CN)_5]$ .  $2NH_3$  as an unstable solid. The corresponding tetraethylammonium salt when treated with acetic acid in acetonitrile converts it into a blue coloured complex,  $(Et_4N)_2[FeNO(CN)_4]$ . 29

B- THE STRUCTURAL CHEMISTRY OF NITROSYLCYANO COMPLEXES

Since the emphasis in this thesis is on the chemistry of "Nitrosyl Complexes of Monovalent Chromium," which was explore using some substitution reactions, it is proper to discuss briefly different physico-chemical methods employed so far for the elucidation of the structural aspects of the starting complex along with the trends observed with the alike complexes of the other transition metals. The shapes of the complex ions are of great interest which can account for an indication of the relative strengths of chemical reactivities in these complexes (vide infra). Therefore some general comments on results of X-ray diffraction studies, magnetic measurement studies along with e.s.r. spectra, redox properties, vibrational spectra, electronic spectra and photoelectronic spectra are reviewed here.

# (i) X-ray Diffraction Studies:

The representative nitrosyl cyano complexes whose structural analysis have been made are presented in Table 2. Interestingly in all these complexes, the M-N-0 angle nearly approaching to 180° and hence the M-N-0 group attachment is linear. Among the hexacoordinated complexes the shortest M-N distance is found for (FeNO) 3+ group and the largest has been encountered for (CrNO) 2+ group considering the first transitional series. The

Table-2

Compound	(A)	N con (A)	Reference
K3[VNO(CN)5].2H20	1.66	1.29	22
K4[VNO(CN)6].H20	1.686	***	11
K3[C=NO(CN)5].H20	1.99	1.21	33
[Co(en)3] [CrN0(CN)5].2H20	1.71	1.21	30
K3[MmNO(CN)5].2H20	1.66	1.21	31
Na <sub>2</sub> [FeN0(CN) <sub>5</sub> ].2H <sub>2</sub> 0	1.63	1.13	32
(Etan)[Feno(CN)4]	1.56	1.16	29
K4[MONG(CN)5]	1.95	1.23	20
(PPh4)3[MoNG(CN)5].2H20	1.921	1.195	26
and the same and t	and an along along the a		

reported C-N distance for all these complexes is of constant value whereas for the N-0 distance one can observe some variations. The expected trend is observed for the (MoNO) + and (MoNO) 2+ groups with respect to Mo-N and N-0 bond distances. The insensitiveness of C-N bond distance is suggestive that stabilization of the metal is mainly done by the nitrosyl group. Quite expectedly vibrational spectroscopy can explain this trend along with the changes in N-0 bond distance (vide infra). The pentacoordinated complex containing (feNO) 2+ group has a tetragonal pyramidal structure. The short Fe-N distance is suggestive of strong trans directing effect of the coordinated nitrosyl group and by virtue of this effect, the compound was isolated at low pH. 29 The only known heptacoordinated complex is pentagonal bipyramid in nature and though the stability of this compound was sometimes thought unusual which can now be explained easily on the structural data in the bonding scheme (vide infra).

# (ii) Magnetic Measurement Studies:

In advancement of bonding scheme of nitrosyl complexes (vide infra), the observed magnetic moment values are quite expected. Taking into account as metal and nitrosyl group together (because of the fact that nitric oxide is itself paramagnetic with

respect to one unpaired electron), the number of total electrons present in this group are given in Table 3 alongwith the expected number of unpaired electrons and the observed magnetic moment values. The strong covalent nature of M-NO bonding is now certain from the studies of other physico-chemical measurements and X-ray structural analysis. The bonding scheme presented in Fig. 1(b) shows the nature of this interaction and though cyanide group in most of its complexes behave as a good x-bonding ligand, in cyanonitrosyl complexes the strong interaction between metal ion and nitrosyl group is enough to cause the separation of bonding, nonbonding and antibonding orbitals to a large extent. In these hexacoordinated complexes maximum symmetry expected is C4v leading to a strong tetragonal distortion. Thus the ordering of these orbitals according to Fig. 1(b) is  $(2e) < (1b_2) < (3e)$ . The bonding orbital below '2e' will accommodate the ligands electrons. Thus filling up of the 'd' electrons on the metal will start from '2e' level. Rationalization of the bonding scheme has been done mainly on the consideration that the nitrosyl ligand is formally considered as N≡0+. This assumption is only to accommodate the nature of the X -bonding which is vital to the linear mode of NO coordination. From the valence bond picture, the

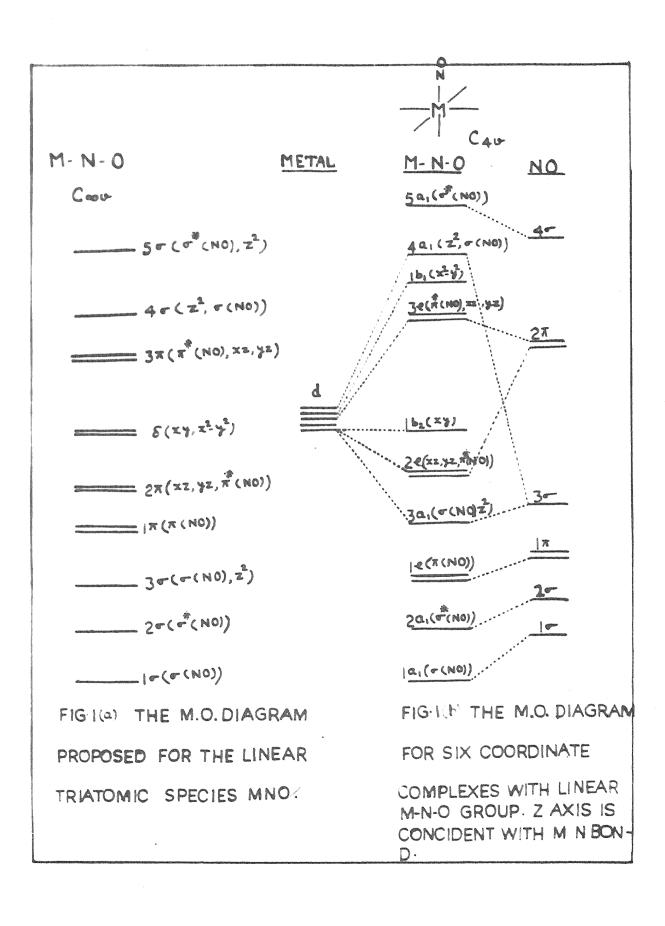


Table-3

Compound	Electron configuration (MNO)	'number '	mag.mom spin on value	d 10bserved ent mag. Ly moment (BA)	Ref.
K3[VNO(CN)5].2H2	{VNU} 4	0	0	D	21
K4[VNG(CN)6].H20	{VNO3 4	0	0	D	10
Ka[CrNO(CN)s].H20	{CrNO} 5	1	1.73	1.87	19
K4[CxN0(CN)5].2H20	{CrNU} 6	0	0	D	23
K3[MnN0(CN)5].2H20	{MnNU} 6	0	0	D	27
K2[AnNO(CN)5].2H20	{mnN0} 5	1	1.73	1.73	27
Na2[FeNO(CN)5].2H20	{FeNO} 6	0	0	D	27
(Et <sub>4</sub> N)[FeNU(CN) <sub>4</sub> ]	{FeNO? 7	1	1.73	1.75	28
K4[mone(cn)5]	{mono} 6	0	0	D	17
(PPh4)3[MOND(CN)5].2H20	{mono} 5	1	1.73	1.96	26

n = number of electrons in 'd' orbital; D= diamagnetic.

bonding of NO to transition metal ions can be treated by several possible ways which are shown below:

Linear I Bent II III Bridging IV

Keeping this view in mind it is worth mentioning that the NO+ formalism in general is merely an useful consruct and the oxidation state formalism and the electron neutral approach are not intended as substitute for detailed bonding descriptions. In this regard keeping the metal nitrosyl component as an inseparable entity,  $\{MNO\}^n$  (n = number of 'd' electrons present in the metal ion considering coordinated NO as NO+) nomenclature is a practical approach. 51 In this formalism the cyanonitrosyl complexes may contain the electronic configuration {MNO} n, where the value of n may be 4,5 or 6 which directly count the number of 'd' electrons. Obviously complexes containing n = 4 or 6 will show diamagnetism and for n=5 paramagnetism with respect to one unpaired electron is expected. The magnetic moment values are presented in Table 3.

For the complexes containing d<sup>5</sup> configuration, the

spinorbit coupling constant would contribute in the measured magnetic moment value. The spin-orbit coupling constants for No(I), Nn(II) and Cr(I) are -450, -300 and -190 cm-1 respectively, which will affect the magnetic moment values a bit greater than the spin only value at room temperature.  $^{57}$ The observed results for the chromium and molybdenum complexes described here follow this trend. However, for the manganese complex the magnetic moment measurement of  $N_2[MnNO(CN)_5]$  in solution gives the value corresponding to spin only formula. Interestingly the magnetic moment value of its silver salt, measured in the solid state gives a sub-normal magnetic moment value of 0.55 B.M.  $^{27}$  only. The reason for this anomaly is difficult to explain.

# (iii) Infrared Spectroscopy:

Recent X-ray studies has described in Table 2 revealed the presence of linear M-NO group and thus the coordinated NO group can be regarded as  $NO^{\dagger}$ . Thus infrared spectra of this series of complexes are widely used to obtain the information about the nature of metal to ligand bonding. Although much is known about the nitroyal stretching frequency that is the nature of ligand vibration, it is only recently that some efforts are made to locate the associated N(M-NO) and N(M-NO) modes.

Characterisation of these low frequency vibrations would reflect more directly to the state of the metalligand bonding. The first meaningful work on this aspect is done by During and coworkers on the hexacoordinated ruthenium nitrosylhalo complexes down to the frequency of 50 cm 1. Contrary to the carbonyl compounds the )(M-NO) and  $\delta$ (M-N-O) in general appear to low intensity and thus possess additional problem. Furthermore, dealing with the hydrated salts of cyanonitrosyl metallate, considerable difficulties are encountered in localing these vibrations because of the presence of librational modes due to water and vibrations due to >(A-CN) and δ(M-C-N). Recently to avoid the complexity due to the presence of water of crystallization, infrared studies are made on unhydrous complexes Table 4. For the relative position between the metal-nitrogen stretching and metal-nitrosyl deformation mode, assignments are made from deducing the results obtained from the studies of carbonyl and cyano complexes. In metal carbonyl complexes  $\mathcal{V}(\mathbb{N}-C0)$  is lower than  $\delta(\mathbb{N}-C-0)$ . The same order is usually obtained for complexed cyanides. However, unequivocal assignment of these vibrations require 15N and 13C substitution data along with Raman polarization data. Some of the work on 15N substitution are done by Miki and coworkers. 41 Using a linear three-body model, they assign

Table-4

Infrared spectral data of the cyanonitrosyl anions in the solid state (in  $cm^{-1}$ ).

patinh estato éstato quiligo escolo apricir escolo aprilido asrola casalo.	estata egitika gyada esates enistra ekistra	degree stille stille stille	CONTRACTOR STATES AND STATES	portes appido challo Adjub	MARKE MARKE evine etika
Compound	)(CN)	J(NO) 8(	M-N-0)	J(11-11)	Ref.
appears success appears and appears ap	queens queens aprillar socials queen doors	Applie ettete ettete i	decide states entres weigh	spinios etiopis dipota soluta	unitato episido adicirio bacido
K3[V(CN)5N0].2H20	2105, 2080	1530	CORP	4000	22
K4[V(CN)6NB].H2B	2095, 2100	1508	631	620	10
K3[Cr(CN)5N0].H20	2020, 2120	1630	612	621	35
K4[Cr(CN)5ND].2H2D	2095, 2077	1470	627	645	35
K3[Mn(CN)5N0].2H20	2124, 2129	1706	660	660	36
K2[Nn(CH)5NO]	2150, 2100	1885	550	628	27,37
Na <sub>2</sub> [Fe(CN) <sub>5</sub> NO]	2144, -	1940	663	496	34
(Et <sub>4</sub> N) <sub>2</sub> [Fe(CN) <sub>4</sub> NC]	2111, 2122	1755	squaler	<b>***</b>	29
K4 [MO (CN) 5NO]	2120, 2106, 2097, 2080	, 1450	589	604, 595	35
(PFh <sub>4</sub> ) <sub>3</sub> [Mo(CN) <sub>5</sub> NO]	2040, 2023	1580	ignation	easte	26
					anna desta desta

the higher wave number band to the M-N stretching vibration and to the lower one M-N-0 bending vibration in the lower frequency range. These assignments are definitely more realistic than the assignments done on tentative basis as presented in Table 4. The work of Miki and coworkers on cyanonitrosyl metallates are summarized in Table 5.

Taking representative example as ammine complexes,  $\mathcal{D}(\text{M-NH}_3)$ , a 'single bond'-stretching frequency appears much lower 42 than those appeared for  $\mathcal{D}(\text{M-NO})$  inspite of the fact that the mass of the NO group is larger than NH3 group. This represents considerable x-backbonding in nitrosyl complexes (vide infra).

# (iv) Electronic Spectra:

Attempts to correlate the structural information with a unified description of the bonding in metal nitrosyl complexes formally remain not much of significance. This is due to the fact that the inherent question, still, lies on the fact that where nitrosyl group is positive or negative which means how many 'd' electrons are present in the compound? Till date we donot have any formal answer to this problem regarding the formal oxidation state of the involved metal ion. It is only in the first half of this decade that a meaningful alternative description of the bonding in

obles.

- Pattoring		TV Com		75 FO 00	10 Jex	14. NO COMDIEZ	Reference
		V(M-M)	)(NO) /(M-N) 6(M-N-O)	( ) ( ) ( )	(HO) V(m-H)	S(M-M-0)	
20	1643,	k -	610	1610,	617	009	OH
K3 [Mn (CH) NO] RH O	1741	663	60 60 60 80 60 80	1704, 1694	099	651,	7
K <sub>3</sub> [Mn (CH) 5 No]. 2D 0	1736,	663	663,	•	9	•	14
Kg[Mn(cm) mo]	1711,	629	659	1675,	199	648	7
Ag_[Wn(CH) HO]	9888	628	628	1850	620	620	7

metal-nitrosyl complexes is developed. This is originated from the pioneering analysis of the structures of the triatomic species of the non-transition elements using the correlation method by Walsh, 45 which was first developed by Hund 46 and Fulliken 47 for distance molecule. Walsh's study is concerned with triatomic species which has only s and p orbitals in the valence shell of the atom and suggested that the concept should be generally applicable. Mingos and Ibers 48 have first applied this concept to understand the M-N-0 angles in the metal nitrosyl complexes and Pierpont and Eisenberg 49 and Mingos 50 have utilized these concept in attempt to interprete the geometry of the tetragonal nitrosyl complexes. In a six coordinate complex of M-NO group, the maximum symmetry is CA, and accordingly the modification of the molecular orbital diagram for the linear triatomic species PNO will change in FNOL, symmetry as shown in Fig. 1. In the molecular orbital diagram (Fig. 1b) the orbital 3a, is primarily localised on the N-atom of the NC ligand and is o -bonding with respect to MND group. The degenerate 2e orbital is bonding with respect to M and N and antibonding between N and O. The 1b, orbital is localised on the metal dxv and is nonbonding. Thus an ANU complex with electronic configuration (3a4)2(2e)4 has three bonding interactions between the metal and NO group which is similar to the

backbonding concept. The presence or absence of electron in the 1b<sub>2</sub> orbital will affect very little in deciding the nature of bonding of the M-NO group.

It is experimentally difficult to know the ground state configuration of the diamagnetic complexes in this series. However, e.s.r. technique has been widely employed to investigate the ground state electronic configuration of paramagnetic complexes, especially K, [Cr(CN), ND] . Though there is not complete agreement on the interpretation of the e.s.r. data of this complex made by several groups, yet the successful explanation of most of the e.s.r. parameters is consistent with the assignment of the  $2_{\mathrm{B}_2}$  ground state expected from the electronic configuration (2e)4(1b2)1 Mancharan and Gray 43,44 using the information from the known crystal structure of Na\_[Fe(CN)\_N0].2H\_20 32 assign the observed electronic transition of a series of cyanonitrosyl complexes. Though the agreement between the observed electronic transition energies and the calculated one electron energies is not very good, yet the model they have used can accommodate a wide variet of experimental facts is interesting. The obtained results of Mancharan and Cray are shown in Table 6.

Table-6

Elec	tronic spectra	of [M(CN)5	[0] n- in aqueous solution	
Complex	Observed maxima Max (cm <sup>-1</sup> )	Calculated energies (cm <sup>-1</sup> )	Band assignments	Ref.
[V(CN)5NO] 5*	12,900 1.15	9,200	$^{1}A_{1} \rightarrow ^{1}E (2b_{2} \rightarrow 7e)$	
	21,160 36.5	19,000	$^{1}A_{1} \rightarrow ^{1}A_{2} (2b_{2} \rightarrow 3b_{1})$	
	32,470 ~1000	30,100	$^{1}A_{1} \rightarrow ^{1}A_{1} (6e \rightarrow 7e)$	43
	37,470 ~5200	23,260	$^{1}A_{1} \rightarrow ^{1}E (2b_{2} \rightarrow 8e)$	
[cr(cN)5N0]3-	13,700 8	12,660	$^{2}\text{B}_{2} \rightarrow ^{2}\text{E} (6e \rightarrow 2b_{2})$	
	15,380 ~1.5	13,890	$^{2}\text{B}_{2} \rightarrow ^{2}\text{E} (2b_{2} \rightarrow 7e)$	
	22,200 72	26,550	$^{2}\text{B}_{2} \rightarrow ^{2}\text{B}_{2} (6e \rightarrow 7e)$	43
	27,320 59	28,260	$^{2}\text{B}_{2} \rightarrow ^{2}\text{B}_{1} (2\text{b}_{2} \rightarrow 3\text{b}_{1})$	
	37,300 1100	37,420	$^{2}\text{B}_{2} \rightarrow ^{2}\text{E} (5e \rightarrow 3b_{2})$	
	43,480 3600	35,680	$^{2}$ <sub>B<sub>2</sub></sub> $\rightarrow$ $^{2}$ E (2b <sub>2</sub> $\rightarrow$ 8e)	

Contd....

[mn(CN)5NO] 3-	18520	22.2	14,700	$^{1}A_{1} \rightarrow ^{1}E (2b_{2} \rightarrow 7e)$	
	24,690 ~	-60	24,200	$^{1}A_{1} \rightarrow ^{1}A_{1} (6e \rightarrow 7e)$	
	28,980	111.4	26,500	$^{1}A_{1} \rightarrow ^{1}A_{2} (2b_{2} \rightarrow 3b_{1})$ 4:	3
	37,850	4000	37,770	$^{1}A_{1} \rightarrow ^{1}E (6e \rightarrow 5a_{1})$	,
	42,550 ~	4500	41,490	$^{1}A_{1} \rightarrow ^{1}E (6e \rightarrow ^{3}b_{1})$	
	45,450 ~	-5000	40,470	$^{1}A_{1} \rightarrow ^{1}E (2b_{2} \rightarrow 8e)$	
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[mn(CN)5NO] 2-	12,050	19	7,820	$^{2}\text{B}_{2} \rightarrow ^{2}\text{E} (6e \rightarrow 2b_{2})$	
	18,600	20	18,350	$^{2}\text{B}_{2} \rightarrow ^{2}\text{E} (2\text{b}_{2} \rightarrow 7\text{e})$	
	25,960	1700	26,170	$^{2}\text{B}_{2} \rightarrow ^{2}\text{B}_{2} (6e \rightarrow 7e)$	
	28,570	120	32,530	$^{2}\text{B}_{2} \rightarrow ^{2}\text{B}_{1} (2\text{b}_{2} \rightarrow 3\text{b}_{1}) $ 4:	3
	32,280	880	28,830	$^{2}\text{B}_{2} \rightarrow ^{2}\text{E} (5e \rightarrow 2b_{2})$	
	37,030	2400	38,740	$^{2}$ E <sub>2</sub> $\rightarrow$ $^{2}$ E (6e $\rightarrow$ 5a <sub>1</sub> )	
	48,540	23800	45,050	$^{2}B_{2} \rightarrow ^{2}E (2b_{2} \rightarrow 8e)$	
there there was the week the first	and Across Holosop editors epic	dis agrees access sa			
[Fe(CN)5NO]2-	20,080	8	20,540	$^{1}A_{1} \rightarrow ^{1}E (2b_{2} \rightarrow 7e)$	
	25,380	25	25,090	$^{1}A_{1} \longrightarrow ^{1}A_{1} (6e \longrightarrow 7e)$	
	30,300	40	30,770	$^{1}A_{1} - ^{1}A_{2} (2b_{2} - 3b_{1})$	A
	37,800	900	37,750	<sup>1</sup> A <sub>1</sub> <sup>1</sup> E (6e 5a <sub>1</sub> )	
	42,000	700	37,750	<sup>1</sup> A <sub>1</sub> <sup>1</sup> E (6e 3b <sub>1</sub> )	
	50,000	24000	4,900	<sup>1</sup> A <sub>1</sub> <sup>1</sup> E (2b <sub>1</sub> Be)	

<sup>\*</sup> see reference 22.

# (V)X-ray Photoelectron Spectroscopy:

The X-ray photoelectron spectra may be used for studying the chemical bonds in the coordination compond owing to the fact that the binding energy Eb of the inner shell electrons depends upon the effective charge q. The binding energies of electrons of the atoms in chemical compound are usually characterised by the changes (shifts  $\triangle$  E) of these energies in the compound studied compared to the energies in the reference compounds. Free atoms are often used as reference compounds. Under these conditions a postive shift corresponds to the positive effective charge of the atom in the compound under study and the negative shift corresponds to the negative charge. The direct correlation of the atomic charge and the shift is a simplified procedure.

The effective charge of the NO group has been discussed for over two decades. 54 This anomaly in this field is due to the fact that the actual electron density distribution is rather far from both limiting descriptions, NO<sup>+</sup> and NO<sup>-</sup>, and the absence of the clear cut physical concept of the exidation state in this case may give rise to apparent contradictions. The exidation states of the metal atom for the sign of the charge of the NO group are determined by evaluating how close certain physico-chemical characteristic of the nitrosyl compounds are to those of the above limiting cases. These characteristics are sensitive to various aspect

of the electron density distribution so that the boundary between the NO and NO cases depends on the characteristic considered and the problem concerns only the definition of the oxidation state concept rather than the measurement of a physically observed parameters. Thus the closest correspondence to the classical chemical concepts, for example, the oxidation state of a metal atom, may be obtained with such observable parameters which describe the extent to which the electron density is drawn away from an atom or a group.

The  $N_{1S}$  value for  $N0^+$  in  $N0C10_4$  is about 409 eV and 406 eV is for the neutral molecule. The extrapolation of the data for  $N0^+$  and N0 yields the range of  $N_{1S}$  value for  $N0^-$  in the vicinity of 402 eV.

Folkesson 52 started a systematic photoelectron spectral study for a series of a nitrosylcyano complexes. The results are tabulated in Table 7. The N<sub>1s</sub> binding energies for the cyanide group in this series reflect the observation made by  $\mathcal{N}(CN)$  in infrared spectroscopy as discussed earlier. Interestingly most of the N<sub>1s</sub> binding energy forthe nitrosyl group falls below 402 eV and hence can be treated containing the nitrosyl group NO<sup>-</sup>.According to the arguments put before, the nitrosyl group in nitroprusside can be said to contain a formally positive charged N that is NO<sup>+</sup>. However, these data are insufficient

in the sense that they do not say anything about the binding energies of the metal electrons. A comparison of a series of a particular metal in its complexes containing different exidation states having the same coordination number would have been more useful in assessing the charge distribution. Furthermore, the ESCA data of a nitrosylcyanometallate ions in its consecutive reduced or oxidised form, as in some cases it is formed, would supplement the study. The first point of the above views has been studied by Nefedov 55 where he compared the Fe<sub>2n 3/2</sub> energies in Na<sub>2</sub>[Fe(CN)<sub>5</sub>NO],  $K_5$ [Fe(CN)<sub>6</sub>] and  $K_4$ [Fe(CN)<sub>6</sub>]. These data are presented in Table 8. alongwith the data for Fe(h5-CgHg)2. The trend in Fe 2p3/2 according to the above table suggests that iron in nitroprusside is in highly oxidised state compared to even that in  $K_3$  [Fe(CN)<sub>6</sub>] meaning thereby the formal oxidation state of iron in nitroprusside would be IV. Furthermore in the absolute sense the N4. binding energy for NG is even lower for the neutral NO molecule suggesting that the coordinated nitric oxide even in nitroprusside should be treated as NOT.

1414

Attempts have been made by Sarkar and Muller  $^{26}$ ,  $^{53}$ ,  $^{56}$  to observe the changes appeared in the two adjacent reduced and oxidised species of nitrosyl complexes of molybdenum. This has been done on the ground to observe the changes occur in the  $3d_{3/2}$  and  $3d_{5/2}$  binding energies

Table-7.

ESCA data of some of the cyanonitrosyl complexes

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Compound	Eb N <sub>1s</sub> (NO)	Eb N <sub>1s</sub> (CN) eV	Electron configu- ration {MNO} n	Reference
[ v(cn) 5 No] 3-	400.6	398.8	{VNU} 4	52
[Cr(CN)5NU]3-	401.4	399.0	{CrNO} 5	52
[ Mm (CN) 5NO] 3-	401.6	398.3	{mnNO} 6	52
[mm(CN)sNC]2-	402.1	398.3	{ΓιηΝΟ} 5	52
[Fe(CM)5N6]2-	403.9	398.7	{FeNO} 6	52
[ Mo(CN) 5 0] 4-	401.1	398.8	{MONO} 6	52
[ Mo(CN) 5NC] 3-	400.1	398.8	{NoNO} 5	26,53

Table-8.

Binding energies (eV) of some iron complexes

	Fe 2p <sub>3/2</sub> (eV)	N 1 S  (eV)	### ### ### ### ### ### ### ### ### ##
Fe(h <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	708.0		55
K4[Fe(CN)6]	708.8		55
K3[Fe(CN)6]	710.3		55
Fe[Fe(CN)5NO]	711.3	402.6	55
Na <sub>2</sub> [Fe(CN) <sub>5</sub> NO]	711.0	403.6	55

of molybdenum alongwith N<sub>4s</sub> binding energy of coordinated NO. For a redox reaction  $\{MoNC\}^n \xrightarrow{-s} \{MoNC\}^{(n-1)}$ (n = number of d electrons) the overall electronic distribution in (MoNO) modety will change. The release of an electron may takes place (a) from the molybdenum ion, (b) from the nitrosyl ligand, (c) an inseparable withdrawal of an electron from both the centres that is from MND group. From the crystallographic data of  $K_{\Delta}[MoNU(JN)_{5}]$  and  $(PPh_{\Delta})[MoNU(CN)_{5}].2H_{2}U$  (vide Table 2). It is known that the Mo-N bond in the oxidised species {MoNO} 5 is shorter than that of the {MoNO} 6 group contain--ing compound. This shortening is due to a stronger MoNO attachment in the former species than the latter. The stronger attachment can only be visualised by the increase back-donation from Mo -> NO, leading thereby accumulation of more electron density on NO. The observed trend presented in Table 6 justifies these arguments. It is interesting to note that there is overall no electronic change of the cyanide groups present as co-ligand in both the complexes.

# (vi) Redox Properties:

The one electron reduction of  $[CrNO(CN)_5]^{3-}$  was first demonstrated by Wilkinson and coworkers. <sup>19</sup> They used the Polarographic method of reduction and could not be able to isolate the oxidised product at

that time. Few years latter, Griffith using same method have been able to isolate  $[CrNU(CN)_5]^{4-}$ . Cotton and coworkers have isolated the oxidised product (one electron) of  $[Mn(CN)_5N0]^{3-}$  using bromine or nitric acid as oxidizing agent. The extrastability achieved by coordinated nitric oxide for a particular metal can be seen from the isoelectronic redox systemfor the manganese complex (Table-9).

<u>Table-9.</u>
Standard electrode potential

Couple	E <sub>0</sub> (V)	Reference
कृतिक व्याप्त प्राप्त प्राप्त व्याप्त	enter distri unio distri enter espera estato entera estato.	eticita dell'oli dell'oli piddig illordio scotto dellino
[CrNO(CN) <sub>5</sub> ] 3-/[CrNO(CN) <sub>5</sub> ]4-	-1.146	58
[mn(CN)6]4-/[mn(CN)6]5-	-1.06	59
[mn(CN)5NO] 2-/[mn(CN)5NO] 3-	+0.597	60

The nitroprusside analogue or rhenium  $^{61}$  shows reduction which is a reversible one as may be expressed:  $[\text{Re}(\text{CN})_5\text{NC}]^{2-} + e^- = [\text{Re}(\text{CN})_5\text{NO}]^{3-}$ Jakob and coworkers studied quantitatively one electron oxidation of  $[\text{Mo}(\text{CN})_5\text{NO}]^{4-}$  which is a reversible one.  $^{62}$  However, several attempts to isolate the oxidised product failed and it is only recently  $[\text{Mo}(\text{CN})_5\text{NO}]^{3-}$  has been synthesized and charactrised.  $^{26}$  A comparative study

of the electrochemistry of  $[Fe(CN)_5NO]^{2-}$  at  $NO^{+}$  itself has been made. 63 The nitrosonium ion shows three reduction waves and these have been interpreted as the formation of NO in the first stage which then dimerized and reduced to  $N_2O_2^{2-}$  in the second prt of reduction. The third phase corresponds to three electrons reduction of NO into  $NH_2OH$ . The  $[Fe(CN)_5NO]^{2-}$  anion first undergoes reduction to  $[Fe(CN)_5NO]^{3-}$  which undergoes either protonation and reduction via second wave or formation of the complex  $[Fe(CN)_5(NH_2OH)]^{3-}$ . Polarographic reduction of nitroprusside yields  $[Fe(CN)_4(NO)]^{2-}$  which has been isolated by the used conventional chemical method. 29 This isolation demands a reinterpretation of the earlier electrochemical studies on nitroprusside anion. 64,65 (vii) Electron Spin Resonance Studied:

Most of the work in this field is related with the investigation of e.s.r. spectrum of [Cr(CN)<sub>S</sub>NO]<sup>3</sup>. Several groups <sup>66-74</sup> have tried to interpret spectrum but there is not complete agreement on the interpretation of the observed data. The important experimental results may be summarised as, an outcome of these investigations, follows: (a) the 'g'- and chromium hyperfine tensor have exial symmetry, (b) the nitrogen hyperfine tensor has slight deviation from exial symmetry which may be comparable to the deviation observed for the CrNO group,

(c) the nitrogen hyperfine tensor is highly anisotropy and gll < gl.

The e.s.r. parameters for other hexa-coordinated complexes of the family  $\left[\text{Cr}(\text{NC})\text{L}_{5}\right]^{75-83}$  are as expected and depend on the electronegativity of L. The 'g' value comes closer to free electron value when there is more delocalisation. This is also reflected in NO stretching frequency.

1.1

The acid hydrolysis of [Cr(CH)<sub>5</sub>NB]<sup>3-</sup> has been foll-owed by e.s.r. method<sup>115</sup> by which it can be shown that the successive replacement of cyanide groups by water takes place.

Some times e.s.r. spectroscopy can affirmly predict the stereochemistry of a complex. This has been exemplified by the study of the oxidised species,  $[\text{Mo}(\text{CN})_5^{\text{NO}}]^{3-}$  which was not isolated at the time,  $^{26}$  but the e.s.r. parameters obtained for the oxidised species in the host of  $\text{K}_3[\text{Co}(\text{CN})_6]$  supports the formation of parent d diamagnetic complex as  $[\text{Mo}(\text{CN})_5^{\text{NO}}]^{4-}$  rather than  $[\text{Mo}(\text{NO})(\text{CN})_5^{\text{COH}}]_2^{4-}$ , which was latter varified by X-ray studies.

The e.s.r. studies on  $[Mn(CN)_5N0]^{2-}$  has been studied in detail 84-87 because of the interest in the ordering of the energy level in the corresponding Cr(I) and Fe(I) complexes. There is controversy existed to attribute the spin density on the N0 group, where one group believe

this due to spin-orbit coupling whereas the other group feels that the spin polarisation mechanism is most likely.

1.8%

1241

Surprisingly Y-radiation of the diatomic  $K_3$  [Mn(CN) $_5$ N0]  $^{86}$  produced the oxidised [Mn(CN) $_5$ N0]  $^{2-}$  species by simple electron addition whereas nitroprusside loses an electron on irradation.

#### C. REACTIVITY OF COORDINATED NITRIC OXIDE :

The study of the reactivity of the nitrosyl complexes compare to the carbonyls are scare. This is due to the fact the coordinated nitric oxide is very firmly bound with the metal and a ligend displacement reactions are not found so commonly as these happen readily with the carbonyls. Due to the enormous studies on the car onyls having industrial significance, in recent years many facets concerning the reactivity of nitrosyl complexes have emerged. Two things are of prime importance in these studies. The first one is to deal with the environmental pollution caused by nitric oxide and the second one is the development of newer catalytic system of industrial applicability.

The reactivity of coordinated nitric oxide falls under the following catagories.

# (a) Nucleophilic Attack:

114

100

This is the most widely known reactivity of nitrosyl complexes which can be classically examplified by the following reaction:

$$[Fe(CN)_5NO]^{2-}$$
 +20H ====  $[Fe(CN)_5NO_2]^{4-}$  +H20 ...(1)

$$NO^{+} + OH^{-} = NO_{2}^{-} + H^{+}$$
 ...(2)

The equilibrium constants for the above two reactions are 1.5X10<sup>6</sup> and 2.3X10<sup>31</sup> respectively which is suggestive

enough to infer that the coordinated NO<sup>+</sup> is a much weaker electrophile than free NO<sup>+</sup>. The corresponding ruthenium and osmium analoges behave similarly. 88,89 A number of reactions are known where a lot of nucleophiles have been used instead of OH<sup>-</sup> and the general reactivity is of the same nature as shown below:

$$PhNH_2 + N0^+ \rightarrow PhNH_2^+ + H_20$$
 (iii)

$$[Ru(C1)(bipy)_2(N_2Ph)]^{2+} + H_2^{0} = ...$$
 (iv)

$$[Ru(NH_3)_5NO]^{3+} + NH_2OH --- > [Ru(NH_3)_5N_2O]^{2+} + H_3O^{+} (v)$$

$$\left( \left[ \text{EN} \left( \text{NH}_{3} \right)_{4}^{2} \text{RuNH}_{2} \left( \text{D} \right) \text{NRu} \left( \text{NH}_{3} \right)_{5}^{5+} \right) \longrightarrow \text{cis-} \left[ \text{RuOH} \left( \text{NH}_{3} \right)_{4}^{2} \text{NO} \right]^{2+} \\ + \left[ \text{Ru} \left( \text{NH}_{3} \right)_{5}^{2} \text{N}_{2}^{2} \right]^{2+} + \text{H}^{+} \quad .. \quad (vi)$$

When  $N_3$  is used the reaction may be depicted as below:  $\left[ \text{RuCl} \left( \text{dipy} \right)_2 \text{NO} \right]^{2+} + N_3^{-} --- \right) \left[ \text{RuCl} \left( \text{dipy} \right)_2 \text{S} \right]^{+} + N_2^{-} + H_2^{-}$ 

where S indicates a solvent molecule.

The formation of the labile [RuCl(dipy)25] thas been synthetically exploited for preparation of [RuCl(bipy)X] nt complexes where Xis a monodentate ligand. 94-98 In a

similar reaction with diarsins complex, the isotopic levelling give soldence for attack of  $N_3^-$  at coordinated NO with the formation of a cyclic  $N_A^-$ 0 intermediate as:

$$\left[\text{RuCl}(\text{diars})_2^{\text{NO}}\right]^{2+} + N_3^{2-} \rightarrow \left[\text{Cl}(\text{diars})_2^{\text{Ru}}\right]^{2+} + N_3^{2-}$$

# (b) Electrophilic Attack:

By the mode of attack it is evident that the activity of the coordinated NO would be associated just in the opposite direction as encountered earlier.

This attack is therefore associated with the nitrosyl complexes where the f-N-C group is bent or in other words the nitrosyl group centains formally NC. The extent of protenation on this group depends on the formal exidation state of the metal and the trends observed are shown below:  $\text{Cs}(\text{Cl})(\text{CO})(\text{NO})(\text{Pi}\,\text{h}_3)_2 + \text{HCl} \rightarrow \text{Cs}(\text{Cl})_2(\text{CB})(\text{HNO})(\text{Pi}\,\text{h}_3)_2(\text{DS},\text{d}^7) \\ \cdots \text{(viii)}$   $\text{Ls}(\text{NO})_2(\text{Pi}\,\text{h}_3)_2 + \text{2HCl} \rightarrow \text{Cs}(\text{Cl})_2(\text{NHCH})(\text{NC})(\text{PPH}_3)_2(\text{DS}^2,\text{d}^8) \\ \cdots \text{(ix)}$   $\text{Ir}(\text{NO})(\text{CH}\,\text{h}_3)_3 + \text{3HCl} \rightarrow \text{Ir}(\text{Cl})_3(\text{NH}_2\text{CH})(\text{Pi}\,\text{h}_3)_2(\text{Ir}^0,\text{d}^9)$ 

The above cited nucleophilic and electrophilic attacks suggest a broad division like the linear N-N-0 group containing NO should be unstable in alkaline medium whereas the

bent N-N-O group containing NO would be unstable in acidic medium. From the synthetic point of view, the cyanonitrosyl complemes prepared in acidic medium (vide supre)should behave like nitroprusside onion and which is infact found to be true. Contrary to this, the cyanonitrosyls prepared using alkaline hydroxylamine method, though somewhat unstable in acidic medium, denot contain bent nitrosyl group (vide supre). Nevertheless, it has been demonstrated recently that complexes containing the same moiety can be isolated in alkaline and in acidic media as well. This once more reflects our latk of understanding about the variation of actual electron density in the linear M-N-O group. Attempts are being made to answer this uncertainity, 101 however, a complete enswer is still unknown.

# (c) Reduction and Disproportionation:

As described earlier (vide supra) that one electron reduction of  $[Fe(CN)_5N0]^{2-}$  gives brown  $[(Fe(CN)_5N0]^{3-}$  which ultimately affords  $[Fe(CN)_4N0]^{2-}$ . The reduction of  $\{Fe^{II}N0\}^6$  moisty has been explained to proceed to  $\{Fe^{II}N0\}^7$  as intermediate in the brown complex which ultimately changes to  $\{Fe^{I}N0^+\}^7$ . 102 The reduction can commonly occurs at the metal centre 103 and there are some example where reduction takes place on the co-ligand sites. 104 In nonprotic media multielectron reduction of  $[Fe(CN)_5N0]^{2-}$  gives  $[Fe(CN)_5N0]^{3-}$ .  $[Fe(CN)_4N0]^{2-}$ ,  $[Fe(CN)_4N0]^{3-}$ ,  $[Fe(CN)_5N0]^{3-}$  and  $[Fe(CN)_5N0]^{4-}$ .

Using dispersed platinum metals oxide for metal gauze as catalyst, the reduction of NO to either ammonia or dinitrogen has been achieved. This heterogeneous reduction is used in treatment of automobile exhaust gas pollution.  $^{106}$  Using some rhodium and iridium nitrosyl and carbonyl complexes mixtures of NO and CO may be disportionated into  $N_2^{\circ}$  and  $CO_2^{\circ}$ .

# (d) Some Other Reactions of Interest:

14:14

It is long known that NG can be inserted into M-C bond . A representative example is  $^{108}\,$ 

$$ZnR_2 + 2 NO \longrightarrow Zn \begin{pmatrix} O=N \\ O-N-R \end{pmatrix} 2$$
 ... (x1) other transition metals have been used similarly. 109

Recently it has been demonstrated that though a coordinated nitrosyl remains intact, yet it can activate the metal centre so that dimethylformamide can be bonded to the metal as carbamido moiety. 110

The use of dinitrosyl molybdenum derivatives have been made forthe clefin metathesis reaction involving the intermolecular exchange of alkylidine units between alkene via cleavage of C=C bond as cocatalyst. 111,112

A very useful synthetic procedure has been observed where coordinated NO may be transferred to the other metal, 113 for example,

$$[co(NC) (DMGH)_2] + [FeCl_2(FPh_3)_2] - + [Fe(NC)_2(FPh_3)_2]$$

+ other Product

Ring strained olefin in the presence of NO gives dinitroso product 114 as shown below:

$$\left[\operatorname{Co}(h^{5}-c_{5}H_{5})\operatorname{NO}\right] \xrightarrow{\operatorname{NO}} \xrightarrow{\operatorname{NO}} \left[\operatorname{Co}(h^{5}-c_{5}H_{5})\left(c_{7}H_{12}\operatorname{N}_{2}\operatorname{O}_{2}\right)\right] \dots \text{ (xii)}$$

# D. SCORE OF THE WORK

The synthesis, bonding and reactivity of the nitrosyl complexes are complexed and varied. Mononitrosyl complexes containing {MNO} n group containing cyanide as coligand are comparatively less explored regarding substitution reactions keeping the (MNO) moiety intact. As described in the preceding part of the chapter, a fairly balanced physicochemical studies along with X-ray structural data are now available, but for accounting the reactivity of these complexes, there are definitely paucity of data compared to other nitrosyl derivatives. Among the cyannonitrosyl complexes it is only introprusside anion which received much attention in all respects.

The compariative rate of attention regarding substitution reaction in nitrosyl complexes containing cyano group as coligand as well as without cyano group are summarised in Table 10.

An examination of the table shows that except for d<sup>6</sup> configuration the cyanonitrosyl chemistry of other electronic configuration is very poorly studied with respect to their reactivity and substitution reactions. As a more general outlook, for the fast development of the nitrosyl chemistry containing electronic configuration d<sup>6</sup> and more lies on the theoretical interpretation regarding the electronic distribution in the MND moiety. This is due

to the fact that on populating electrons in the antibonding orbital (vide supra) cause destabilization of the bonding between metal and nitrosyl centres enhancing thereby the reactivity of the coordinated NO group. Keeping these possibilities in mind different substitution reactions were carried out by changing the substituent coligand to get slight modification of the electronic distribution in the (FNO) group depending on the nature of  $\sigma$ -donor and  $\pi$ -acceptor capabilities of the substituent ligands. These manoeuvring some times lead to restrict the uncontrolable reactivity of the coordinated NO group or the reverse.

1111

-110-11

11,600

0.16

1421

111

that the nitrosyl complexes containing d<sup>6</sup> electronic configuration do not feel any destabilization of that nature as the highest occupied orbital is nonbonding. However maximum studies on this electronic configuration were made on two grounds. Firstly from the theoretical consideration this electronic configuration can act some sort of a base line from which a comparison can be made for the others containing more number of d electrons. Secondly, it is of merely coincidental that nitrosyl complexes of this configuration already existed long back by the celebrated example of nitroprusside and easily recognized a class of nitrosyl ruthenium chemistry

before the bonding scheme are deviced resulting the development of interpretative nitrosyl chemistry on this electronic configuration.

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The existing theories on different nitrosyl complexes do not suggest anything of the d4 and d5 electronic configurations. This is partly responsible for the paucity of nitrosyl complexes with these configurations and when they are recently being explored, gave interesting results. As it is often discussed earlier that in cyanonitrosyl complexes stabilization rests mainly on the nitrosyl group which indicates the cyanide coligand should be mobile in nature and can be displaced by other ligands of interest. A judicious choice of different ligands containing different atoms at donor site would be of much preparative interest and with their nature of perturbation on the (MNO) moisty. One can think a bit differently to see whether a particular condition, for the introduction of nitrosyl group is very much specific or not.

In the preparative sense, no substituted introyal cyano complex of chromium (I) is reported. As acid hydrolysis of [Cr(CN)<sub>5</sub>NO] <sup>3-115</sup> has been followed using e.s.r. technique and also by polarography and optical spectroscopy. it would be of interest to see whether the different equation products can be isolated using nitrogen donors

like o-phen, dipy, Qu, py and picolines. This type of nitrosyl derivatives are mostly known with the ruthen-lum complexes containing d<sup>6</sup> configuration. As d<sup>5</sup> Cr(I) and d<sup>6</sup> Ru(II) complexes contain the highest populated orbital of nonbonding nature, a comparative chemistry in light of bonding theories would be interesting. Furthermore using other donor atoms containing ligand like acetylacetone or dithiocarbamate, the relative chemistry can be explored.

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From Table 10, it is evident that complexes containing  $(CrNE)^{2+}$  moiety are mostly of the cationic type. Anionic complexes is restricted to only on the preparation of  $[CrNE(CN)_5]^{3-}$ . It would be of interest to see whether other anions of different complexing abilities can be synthesized or not. The study of a series of this type of species, if possible, would open a new way to monitor their complexing abilities using e.s.r. technique. A parallel chemistry of the recently reported  $[CrNE(CNS)_5]^{3-26}$  thus can be made in detail. Besides, nonelectrolytic type of complexes containing  $(CrNE)^{2+}$  moiety is unknown. An attempt in this synthetic approach would be interesting the scope.

The complexes thus synthesized would require an attention of reactivity which can be dealt using different physicochemical techniques already in existence. Thus a correlation can be made on the changes noticed with the help of existing theories in hand.

# Table=10.

{MNO}  n = number of 'd'  electrons	Coordination	Relative chemistry with representative known "
d <sup>4</sup> With CN group	6 and 7	Foorly known [VNO(CN) <sub>5</sub> ] <sup>3-</sup> , [VNO(CN) <sub>6</sub> ] <sup>4-</sup>
Without CN group	5,6 and 7	Fairly known [VNO(DTC) <sub>2</sub> ] [MoNO(C1) <sub>5</sub> ] <sup>2-</sup> [MoNOC1 <sub>4</sub> ]. [MoNO(DTC) <sub>3</sub> ]
d <sup>5</sup> With CN group	6	Foorly known [CrN0 (CN) 5] 3-
Bithout CN group		Moderately known, containing [CrNOL 5] 2+
d <sup>6</sup> With CN group	6 man man man man man man man	Well known, [FeNO(CN)] 2- and its derivatives
Without CN group	6	Well known, [RuNOX 5] 2-
d <sup>7</sup> With CN group	5 and 6	Poorly known, [FeNO(CN) <sub>4</sub> ] <sup>2-</sup> [FeNO(CN) <sub>5</sub> ] <sup>3-</sup>
Without CN group	6	Moderately known, [FeNOL 5] 2+

d <sup>8</sup> With CN group	6	Poorly known, [PtNO(CN)5] 2-
Without CN group	5 an	d 6 Widely known, [CoNO(,NH3)5]2+
		[mnNU(C0)4] [Co(NU)L2X2].
d <sup>9</sup> With CN group	, 4940 4400 1 4950	Unknown
Without CN group	a soon soon	Fairly known, [Fe(N0) $_2$ X $_2$ ], [Co(N0)(L)(SR)] $_2$
d <sup>10</sup> With CN group	4	Poorly known, K2[NiNO(CN)3]
Wathout CN group	4	Nost widely known, [Fn(N0)3L] . [Fe(N0)2L2] .
		$[Co(NO)(CO)_{2}U]$ , $[N1(NO)X]_{n}$ , $[N1(NO)L_{2}(X)]$ , $[Fe(NO)_{2}(RNC)_{2}]$

# Chapter II

This chapter describes the analysis of the constituent elements and the procedures for the preparation of complexes followed by their properties.

#### EXPERIMENTAL

A- ANALYSIS OF THE CONSTITUENT ELEMENTS :

## Nitrogen :-

When the compound contained thiocyanate group or ligands like o-phenanthroline, dipyridyl, etc., when a tertiary nitrogen was a member of the ring, the nitrogen content was determined microanalytically by Duma's method.

Carbon and Hydrogen:

Carbon and hydrogen present in the sample were estimated microanalytically.

# Estimation of Chromium :-

For the estimation of chromium as chromic oxide, the compounds were decomposed by heating with alkali followed by dissolving in nitric acid. Chromium was precipitated as chromic hydroxide by means of the slightest possible excess of dilute NH<sub>4</sub>OH. The chromic hydroxide when ignited was converted into Cr<sub>2</sub>O<sub>3</sub>. Repeated heating, cooling and weighing were carried out until weight became constant.

# Estimation of Sulphur :-

An aqueous suspension of the chromium complex containing sulphur was treated with bromine water and the solution was heated on a water bath for complete exidation. Digestion was continued till the solution after evaporation of the excess bromine became perfectly colourless. The solution was then acidified with dilute HCl and the sulphate produced was precipitated by addition of Bacl solution and estimated as usual.

B-PREPARATION AND PROPERTIES OF THE COMPLEXES :
Reagents :-

Reagents used for example, chromium trioxide, hydroxylaminehydrogenchloride, potassium hydroxide, potassium cyanide and ligands were of analytical grade. Deaerated water was used in all operations.

Preparation of potassium pentacyanonitrosylchromate(I)hydrate, K<sub>3</sub> [CrNG(CN)<sub>5</sub>].H<sub>2</sub>D:-

pentacyanonitrosylchromate(I)monohydrate was prepared according to the procedure of Griffith, Lewis and wilkinson and was characterised by elemental analyses and infrared spectroscopy.

Found :

K, 33.8; Cr, 15.1; C,18.05; N, 24.2; H<sub>2</sub>0,5.1%.
K<sub>3</sub>[CrN0(CN)<sub>5</sub>] .H<sub>2</sub>0 requires K,33.8; Cr, 15.1;
C, 17.3; N, 24.2; H<sub>2</sub>0, 5.2%.

B-1 Preparation of dicyanodipyridylnitrosylchromium(I),

[CrNC(CN)2(dipy)] :-

Into a filtered aqueous solution (20 ml.) of potassium selt of pentacyanonitrosylchromates(I)hydrate (1.5 g), a solution of dipyridyl (0.75 g) in acetic acid-water (1:1, 10 ml.) was added. The resulting solution was warmed for 10 min. and diluted with 30 ml. of water when a greenish yellow solid pracipitated. The resulting mixture was freed from liberated

hydrocyanic acid by passing a current of CD<sub>2</sub> through the mixture for an hour and the precipitate was filtered off, washed with water, alcohol and ether and dried in vacuum to a constant weight and analysed. The yield based on pentacyanonitrosylchromate(I) was 80%.

## Found :

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Cr, 18.1; N, 24.2; C, 49.6; H, 2.8% [CrNO(CN)<sub>2</sub>(dipy)] requires Cr, 17.9; N, 24.1; C, 49.7; H, 2.76%.

Freparation of dicyanoprtho-phenanthrolinenitrosylchromium(I), [CrNC(CN)2 (o-Phen)] :-

A fittered aqueous solution (20 ml.) of potassium salt of pentacyanonitro-sylchromate(I) hyrdrate (1.5 g) was added slowly into an aqueous-acetic acid (1:1, 10 ml.) of o-phenanthroline (1.0 g) with shaking when immediate greenish yellow solid started to precipitate. After the total addition, the liberated hydrocyanic acid was driven off in identical fashion as described earlier, and the precipitate was filtered off, washed with water, alcohol, ether and dried in vocuo.

# Found:

Cr, 16.7; N, 22.3; C, 53.5; H, 2.7% [CrNU(CN)<sub>2</sub>(o-phen)] requires Cr, 16.6; N, 22.3; C, 53.5; H, 2.5%.

Preparation of dicyanodi(pyridine)nitrosylchromium(I),

[CrNo(CN)2(py)2]:-

A fittered aqueous solution (25 ml.) of potassium salt of pentacyanonitrosylchromate(I)hydrate (2.00 g) was added into an aqueous-acetic acid (1:1,15 ml.) of pyridine (2.5 ml.). The resulting green solution was immediately diluted with air free water (100 ml.)and the mixture was kept in warm condition. Carbondioxide was allowed to bubble through the solution to chase the liberated hydrocyanic acid when a yellow solid was started to precipitate. After two hrs. the precipitation was completed, which was filtered washed with water, alcohol and other and dried in vacuo.

#### Found :

Cr, 17.8; N, 24.1; C, 48.9; H, 3.6%

[CrNU(CN)<sub>2</sub>(py)<sub>2</sub>] requires Cr, 17.8; N, 24.8;
C, 49.3; H, 3.4%.

Preparation of dicyanobis(quinoline)nitrosylchromium(I).

[CrNU(CN)2(Qu)2]:-

The complex was prepared by following an identical procedure described in the preparation of the corresponding pyridine complex just by replacing pyridine with quinoline and the passing of Ct<sub>2</sub> was continued for a period of 6 hrs. to get the yellow coloured complex.

## Found :

Cr, 13.1; N, 17.7; C, 61.0; H, 3.6%

[CrNG(CN)<sub>2</sub>(Qu)<sub>2</sub>] requires Cr, 13.3; N, 17.9;
C, 61.2; H, 3.6%.

Freparation of dicyanodi(β-picoline)nitrosylchromium(I).

CrNU(CN)<sub>2</sub> (β-picoline)<sub>2</sub> :-

A somewhat identical procedure was followed as described earlier for the preparation of this complex replacing pyridine by  $\beta$ -picoline.

## Found :

Cr. 16.2; C, 52.4; N, 21.8; H, 4.3% [CrNO(CN)<sub>2</sub> (P-picoline)<sub>2</sub>] requires Cr. 16.3; C,52.5; N, 21.9; H,4.4%.

Freparation of dicyanodi (Y-picoline) nitrosylchromium(I),

[CrNG (CN)<sub>2</sub> (Y-picoline)<sub>2</sub>] :-

This complex was also prepared by following an identical procedure described in the preparation of the corresponding pyridine complex just by replacing pyridine by Y-picoline.

## Found :

Cr, 16.2; C, 52.3; N, 21.7; H, 4.3%

[CrNO(CN)<sub>2</sub> (Y-picoline)<sub>2</sub>]requires Cr, 16.3;

C. 52.5; N, 21.9; H, 4.4%.

Properties of the cyano substituted complexes,

[CrNB(CN)<sub>2</sub> L<sub>2</sub>]:-

All the cyano substituted complexes are obtained as yellow highly dispersed solids having slight green tings. They are exceptionally stable in

air and remain almost unattacked in dilute acids or alkalies and decomposed only on warning. Thermally they are also stable and do not show any melting or decomposition upto a temperature of 250°CC (Table-11). All these complexes are slightly soluble in acetonitrile being insoluble in other common solvents. Ligands of good donor capacity like pyridins, dipyridyl or triphenylphosphine could not be accommodated in the sixth position even under drastic sealed tube reaction.

[CrN0(CN)<sub>2</sub>L<sub>2</sub>] + CH<sub>3</sub>I Sealed tube no change.

[CrN0(CN)<sub>2</sub>L<sub>2</sub>] + (CH<sub>3</sub>)<sub>2</sub>SO<sub>4</sub> Sealed tube no change.

Methylation reaction was also found to be unsuccessful when it was carried out using CH<sub>3</sub>I with HgI<sub>2</sub> in sealed tube. Though the products isolated in these reactions showed the presence of methylisocyanide retaining nitrosyl group yet they appeared to contain some decomposed product or unreacted starting compound.

[CrNU(CN)<sub>2</sub>L<sub>2</sub>] + CH<sub>3</sub>I + HgI<sub>2</sub> Sealed tube partial decomposition with no change.

The molar conductance values of practically saturated anlydrous methanol solution (10<sup>-4</sup>A) of these cyanonitrosyl complexes (Table-11) suggest their nonelectrolytic nature.

B-2 Freparation of bis(acetylacetonato)nitrosylchromium(I),
[CrNC(acac)<sub>2</sub>]:-

The complex was prepared by refluxing a mixture of K<sub>3</sub>[CrHo(CH)<sub>5</sub>] (2.0 g) and excess acetylacetone (6 ml.) in an air tight compartment with an intermittent removal of the liberated Hydrocyanic acid by passing dry corbondioxide. After refluxing for 8 hrs., the excess acetylacetone was distilled off and the result ant mixture was cooled in vacuo over solid KuH. Traces of free acetylacetone were removed from the cooled brown mass by repeated was ing with petroleum ether and brown crust was extracted with acetone. On evaporation of acetone, the solution gave brown crystals which were washed with petroleum ether. The crystallization process was repeated thrice. The crystals thus obtained were dried and analysed.

#### Found:

Cr, 18.6; N, 5.0; C, 42.9; H, 8.32%

[CrNU(acac)<sub>2</sub>] requires Cr, 18.6; N,5.0;
H, 8.23%.

#### Properties :-

This nonelectrolytic monomeric complex (Table-11) is soluble in most of the common non-polar organic solvents but insoluble in water. Its stability is comparable to that of  $Cr(acac)_3$  as it remains unaffected by concontrated alkalies or mineral acids in cold and decomposes only on prolonged boiling. This complex does not show any interaction with ethanol suggesting that solvation does not take place at the sixth position. But when it is refluxed with traces of pyridine in ethanol, pyridine shows interaction at the sixth position and this has been demonstrated by e.s.r. spectroscopy (vide infra).

B-3 Preparation of aquobis (diethyldithiocarbamato)

nitrosylc romium(I), [CrN0(DTC)2(H2C)] :-

1.0 0 of

potassiumpentacyanonitrosylchromate(I)dydrate was dissolved in 30 ml. of water and into it an aqueous solution of diethyldithiocarbomate (1.0 g) was added. Into the maxed solution 10 ml. of (1:1) dilute acetic acid was slowly added with stirring and the issuing gas was chased by a current of carbondioxide, whereby, reddish brown precipitate appeared which was filtered under suction, washed several times with water. This precepitate is now extracted with acetone and the red

brown compound was precipitated by adding petroleum ether, washed with petroleum ether, dried and analysed. The yield was appoximately 35%.

#### Found :

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Cr, 13.2; C, 30.1; N, 10.5; H, 5.56%

[CrNO(DTC)<sub>2</sub>(H<sub>2</sub>O)] requires Cr, 13.1; C, 30.3;
N, 10.6; H, 5.5%.

## Properties :-

This complex is soluble in alcohol, acetone and acetonitrile to impart orange red colour and in methanol the complex is found to be non-alect-relytic in nature (Table-11).

B-4 Preparation of disothiocyanatodipyridylnitrosylchromium(I). [CrNU(NCS)2(dipy)] :-

chromate and 3.8 g of potassiumthiocyanate was taken in a beaker and 40 ml. of water was added to dissolve the mixture. 1.0 g hydroxylaminehydrogenchloride was slowly added into the solution with stirring. A vigorous reaction sets in and addition of hydroxylaminehydrogenchloride was cautiously done to control the temperature (further addition leads to the expulsion of NO). After the addition of hydroxylaminehydrogenchloride the reaction mixture was stirred at room temperature for an hr. and any grey colour precipitate was allowed to

Table-11
physical properties

Compound	Colour	∧n √1cm² mole	m.p.	Mol.Wt.
[CxNO(CN)2(dipy)]	Greenish yellow	10.2	>250°C	
[CxNO(CN)2(o-phen)]	Greenish yellow	13.5	>250°C	
[CxN0 (CN)2(py)2]	Yellow	15.2	>250°C	
[CzNO(CN)2(Qu)2]	Brown <b>is</b> h yell <b>o</b> w	8.2	>250°C	
[CxNO(CN) <sub>2</sub> (B-picoline) <sub>2</sub> ]	Greenish yellow	13.2	>250°C	
[CrNO(CN) <sub>2</sub> (Y-picoline) <sub>2</sub>	Graenish yellow	14.3	>250°C	
[CrNO (acac)2]	Brown	13.2	206°C	300
[CxN0 (DTC) 2 (H20)]	Reddish brown	17.3	400e	

dissolve by adding dropwise dilute acetic acid. To the filtered green solution, 0.78 g of dipyridyl dissolved in dilute acetic acid was added, a khaki colour precipitate appeared which was stirred for an hr. at a temprerature around 90°C and filtered. The precipitate was washed several times with dilute acetic acid, finally washed with water, dried in air and recrystallised from methanal-petroleum ether. The yield was approximately 45%.

### Found :

Cr, 14.6; C,40.5; N, 19.7; H,2.1; S, 18.1% [CrNO(NCS)<sub>2</sub>(dipy)] requires Cr,14.7; C,40.7; N, 19.8; H,2.2; S, 18.0%.

<u>Preparation of dithiocyanatoortho-phenanthroline-nitrosylchromium(I), [CrNU(NC5)2(o-phen)]:-</u>

The

corresponding o-phenantaroline complex was prepared analogously as described above just by replacing dip-yridyl with c-phenanthroline. The plive green recrystallised compounds was analysed.

#### found :

Cr, 13.6; C, 44.2; N, 18.3; H,2.1; 5,16.8%

[CrNC(NC5)<sub>2</sub>(o-phen)] requires Cr, 13.8; C,44.4;

N, 18.5; H, 2.1; S, 16.9%.

Preparation of disothiocyantodipyridylpyridinenitrosylchromium(I), [CrNU(NCS), (dipy)(py)] :-

About 0.5 g of dythic cyanatodipyridylnitrosylchromium(I) was dissolved in 15 ml. of acetone and 1 ml. of pyridine was added into it. The solution was refluxed for about 2 hrs. on water both with positive pressure of the inside solvent vapour (using a pool of mercury) and the resultant solution was vacuum concentrated. The product was isolated from the solution by adding petroleum ether as yellow solid which was recrystallised from acetonepetroleum ether mixture. The yield was approximately 75%.

Cr, 11.9; C,47.0; N, 19.2; H, 2.9; S, 14.6%

[CrN0(NC5)<sub>2</sub>(dipy)(py)] requires Cr,12.0; C,47.1;

N, 19.4; H, 3.0; S, 14.8%.

Preparation of discthiocyanatoortho-phenanthroline
pyridinenitrosylchromium(I), [CrNu(NCS)2 (o-phen) (py)]:
The o-phenanthroline analogue of the previous compound iso
was prepared analogously just by taking dithiocyanato
rtho-phenanthrolinenitrosylchromium(I) instead of iso
dithiocyanatodipyridylnitrosylchromium(I) as described earlier. The yellow reprecipitated compound from ace
tonep-petroleum ether mixture was dried and analysed.

### Found :

Cr,11.3; C, 49.8; N, 18.2; H,2.7; S, 13.9% [CrN0(NCS)<sub>2</sub>(o-phen)(py)] requires Cr,11.4; C, 49.9; N,18.4; H, 2.8; S, 14.0%.

Properties of thiocyanato substituted complexes:—
The thiocyanato substituted complexes are greenish yellow to yellow in colour and are highly soluble in alcohal and acetone. Alcoholic or acetone solution of these complexes impart greenish yellow colour and addition of methanolic silvernitrate does not give any immediate pracipitation but on standing silver is deposited. The molar conductivity of [CrN0 (NCS)2 (dipy)] and [CrN0 (NCS)2 (o-phen)] are found to be 15.3 and 12.7 \[ \int \] 1 cm. \[ 2 \] mole \[ 1 \] respectively suggesting that the complexes are nonelectrolytic in nature. The other complexes are also nonelectrolytic in nature (Table-12).

It is interesting to note that complexes of (CrNO) moiety with S- or O- donor are coloured reddish brown whereas when the donor is only nitrogen the colour is predominantly yellow. For mixed carbon-nitrogen donor sites, colour is green.

All the complexes described here are somewhat stable in acids but on treatment with alkali the complexes decompose and the coordinated nitrosyl group changes to  $NC_2$ , which can be tested by using Griess

Table-12.

Physical properties

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	Col. Cut	AM	mole—1	
[CrNE(NCS)2(dipy)]	Khaki	15.3		
[CrNU(NCS) <sub>2</sub> (o-phen)]	Clive green	12.7		
[CrN8 (NCS) 2 (dipy) (py)]	Yellow	13.6		
[CrNG(NCS)2(o-phen)(py)]	Yellow	12.9		
MANUFACTURE ACTUAL ALLEY CHANGE WATER MINTER	ngin aparan magalan sajatan bibasar manan dalaga majatan dansir majatan dajatan dalagan salahan sajatan basar b	andrew adjects officials accord formally regards and officials designs around strain.	n dest dans and same with	

reagent. This suggests that though the well known complex,  $K_3$  [CrN0(CN)<sub>5</sub>].  $H_2$ 0 has been isolated in strong alkali medium, yet depending on the nature of co-ligands the same (CrN0)<sup>2+</sup> moiety is attacked by alkali with the concomitant conversion of coordinated nitricoxide to  $N0_2^-$  as known for introprusside anion (vide-supra).

The physico-chemical aspects of these complexes have been discussed in the chapter of structural chemistry of the complexes.

# Chapter III

This chapter describes the physico-chemical investigations of the isolated complexes.

The studies include magnetic susceptibility, infrared, electron spin resonance, mass, x-ray photoelectron and electronic spectral measurements.

STRUCTURAL CHEMISTRY OF THE COMPLEXES

## A- General remarks :

The structural chemistry of the complexes synthesised during this investigation has been followed by magnetic measurements, infrered, electronic, electron spin resonance, X-hay photoelectron and mass spectral studies.

The group (Cr.t.) <sup>2+</sup> contains d<sup>5</sup> electronic configuration and thus this entity is of substantial importance for magnetic properties. Bue to the strong tetragonal distortion of the complexes containing this group, e.s.r. measurement would be of great help in ascertaining the comparative complexing ability of the used X- honding ligands as substituent and also would reflect a nature of charge distribution within (CrNe) group.

Although, no detail magneto-chemical calculations regarding the bonding scheme of the prepared complexes containing (CrNt)<sup>2+</sup> moiety surrounded by different donor atoms is possible using the lifted nature of measurements done here, yet on synthetic point of view the proper characterisation of the sites of coordination can be made with certainty.

The above mentioned conclusion can be amply supported by the other physico-chemical studies made in this investigation.

#### B-Experimental:

#### Conductance measurements :-

The conductivity was measured in analytical reagent grade methanol using a dip type cell with the help of philips conductivity bridge apparatus in the usual manner.

### Magnetic susceptibility measurements :-

Gouy method was used for magnetic measurements. A magnetic field strength of 8500 gauss was employed. The apparatus was calibrated using cobalt mercury thiocyanate. XM (corrected molar magnetic susceptibility) values were obtained by using usual diamagnetic correction as given by figgis and Lewis 116.

Infrared spectral measurements:-

These spectra were recorded over the range

4000 - 400 cm<sup>-1</sup> using a Perkin Elmer infra-cord or

Perkin Elmer- 621 or Perkin Elmer- 377 spectrometer.

Spectra were taken in potassium bromide discs.

### Electronic Spectral Measurements :-

The electronic and reflectance spectra were recorded in spec grade ethanol and nujol mulls respectively with the help of a carry - 14 spectrometer.

Electron spin resonance spectral measurements:

e.s.r. measurements were carried out on either solutions or powdered samples. The parallel and

perpendicular components of the 'g' value were obtained by measurement using potassium bromide as diluent. These measurements were done using a varian- 4502 spectrometer and DPFH was used as internal standard.

### Mass spectral measurements :-

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mass spectrum of [(CrNO (acac)<sub>2</sub>] was measured using an Atlas -CH4 mass spectrometer. The complex is directly introduced into the ion source and heated to a temperature of 210°C.

### X-ray photoelectron spectral measurements :-

The photoelectronic spectrum for [CrNO (acac)<sub>2</sub>] was recorded using ESCA-3 type spectrometer of vacuum generators. It is obtained using Al- KX radiation (1846.6 eV) at a pressure between 5x10<sup>-9</sup>-1x10<sup>-8</sup> torr. The sample was mounted on gold planchettes. The binding energy reported was standardised using a C(1s)binding energy of 285.0 eV.

### C-Results and Discussion :

### Magnetic measurements :-

It has been well established that even in pentasquo complex containing the group  $(CrNO)^{2+}$ , that is,  $[CrNO(H_2O)_5]^{2+}$  is paramagnetic with respect to one unpaired electron. The ligands involved in the preparation of the complexes in this investigation are mostly  $\chi$  - bonding type and thus it is expected that these complexes should be of low

spin type containing only one unpaired electron. The magnetic susceptibility values of the compounds described earlier, have presented in Table-13. The magnetic susceptibility values of the established complexes containing this group are also included here for comparison. This group are also included here for comparison. This indicates paramagnetic range from 1.60 B.M. to 1.74 B.M. for these complexes. The complexes of the type [CrL<sub>5</sub>No] <sup>n±</sup> containing (CrNo)<sup>2+</sup> group show magnetic moment values slightly higher than the values obtained for these complexes.

An examination of the magnetic susceptibility values of several known compounds (Table-13) shows a slightly higher magnetic moment for one unpaired electron (1.73 B.M.) from the spin only formula. This high moment has been explained satisfactorily by Griffith and coworkers 19 to show that this is due to spin and arbital interaction in these complexes.

It is remarkable to point out that all the previously known compounds of this group are hexacoordinated where as the cyanonitrosyl complexes described here are all pentacordinated. In the nitrogen donor ligands irrespective of monodenate or bidentate or bulkiness of the ligands, the complexes are highly insoluble in common solvents suggesting polymeric nature. The magnetic moment values of these complexes are significantly lower

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# Magnetic properties

<b>Compound</b>	Physical state	Ġ B	Temp. K g Xx10-6 Xx10-6	2X X 40-6	Dismagneticx, x10-6 correction Mx10-6 x10	× × ×	neff in B.H.	Het.
K, [Crio (Cr), ].I.o	50116	32	10 cts cas cas tas tas cas cas cas			, cas me ear (\$5 de de de debet)	1.87	19,23
Crwo (wm ) [ ] C m o	S <b>011</b> d	8		0			ري د د	23
[C-MO(H,0),](ClO,)	aqueous	83	0	•	8	9	2.5	23
[Crato (Cat) (0-phen)]	solution solid	303	3.14	985.96	164.00	1149.96 1.67	1.67	
Carro (Car) (Cityy)		<b>113</b>	8	907.70	11.00	1048.70 1.60	1.60	
[Crito (Cit) (py)]	do:	**	3,23	943,16	134.00	1077.16 1.62	1.62	
[crito(ca),(ca),]			8	925.12	211.00	1136.12 1.66	1,66	
[crito(di) (\beta-picoline)]		8	2.00	902.40	163.60	1066.00 1.61	1.61	
[Crito(Cit)2(Y-picoline)2]	dier die	<b>S</b>	8	908.80	163.60	1072.40 1.62	1.62	
[CMO(DTC),(E,0)]			2.62	1037.52	196.40	1233.92 1.73	1.73	
Crac(acae),	8	\$	19.00 10.00 10.00	1106.00	4.00	1000.00 1.79	2.70	
[CrHO(HCS),(dipy)]		3	3.01	1065.54	177.00	1242.54 1.74	1.7	
[(ch((dt))(s)]	*	*	0.33	1004.56	226.00	1230.56 1.73	1.73	
[CrW0(NCS), (0-phen)]	*	**	2.72	1024.38	200.00	1224.38 1.73	3 1.73	
[Criff (if Cs) (o-up on) (Pv)]	*	2	2,2	987,12	249.00	1236.12 1.74	1.74	

then the acetylacetonato derivative. The wide variation of the nitrogen containing ligands as said earlier suggested that the polymerisation is not encountered with these ligands as bridging group. It is interesting to note that the corresponding thiocynato complexes are monomeric ( vide infra) and their magnetic moment values are close to spin only formula. The infrared spectroscopic results which will be discussed below, ruled out the possibility of nitrosyl group interaction or in a bridge position in these substituted cyano complexes. The alternative possibility of bridging via cyano group is solved using infrared spectral measurements.

### Infrared spectroscopy :-

The infrared spectra of the complexes described here and of some of the established complaxes containing the  $(CrNL)^{2+}$  group are presented in Tables-14,15,16 and 17. A comparison between the starting pentacyanonitrosylchromate(I) anion and its derivatives suggested the appearance of a very strong band in the region 1692-1708 cm<sup>-1</sup> in these derivatives are coordinated nitric oxide stretching.  $^{23}$ ,117 The shift of  $\sim 50$  cm<sup>-1</sup> for O(NO) in these complexes compared to the parent compound is in agreement for the nonelectrolytic nature of these complexes where the overall negative charge on the complex is absent compared to the parent anion.

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Important I.R. Spectral bands and their assignments

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Compounds	(OM)(	(B)/	( ( ( C ) ) / ( C )	(0,20)	Reference
K CMO (C) Son o	34549	2137s+	MOZ 9	610	23.8
[CrNO(C1)(d1 ars)2]C1014	1690vs	100/200			117
[ crno(mm <sub>3</sub> ) <sub>5</sub> ]cn <sub>2</sub>	1670vs				8 60 8
[ crwo(m_20)5]cn_2	1747VS				8
[Crwo(Meon)5]Cl2	171975				<b>S</b>
[crao(stos),]a,	1718vs				238
[cr(ono) no(py)3]	1708vs				235
)					

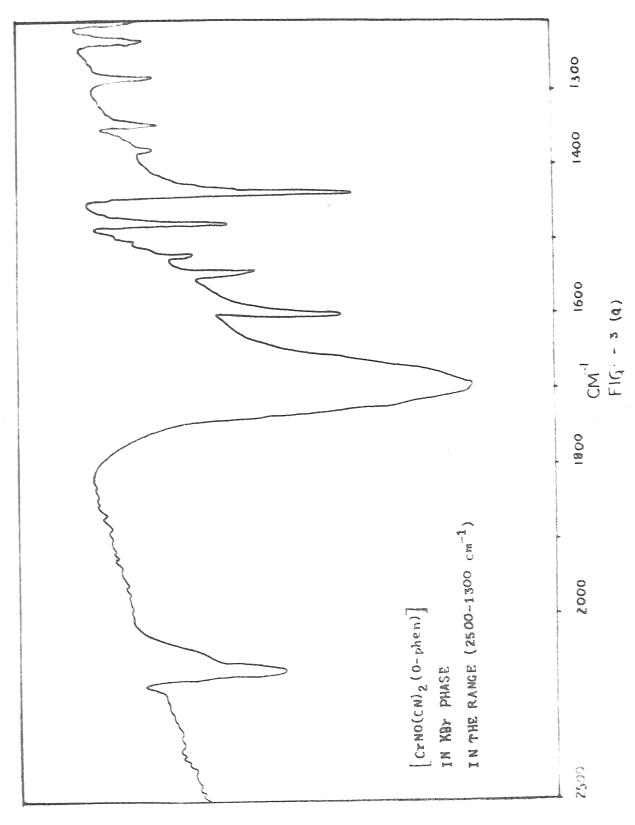
-cm ) and relative intensities(vs,very strong; m, medium; v, weak; sh, shoulder). Positions (

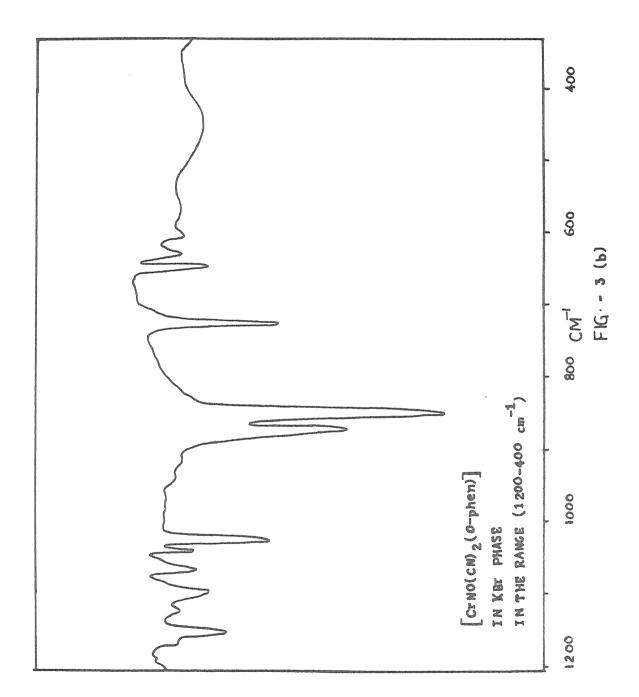
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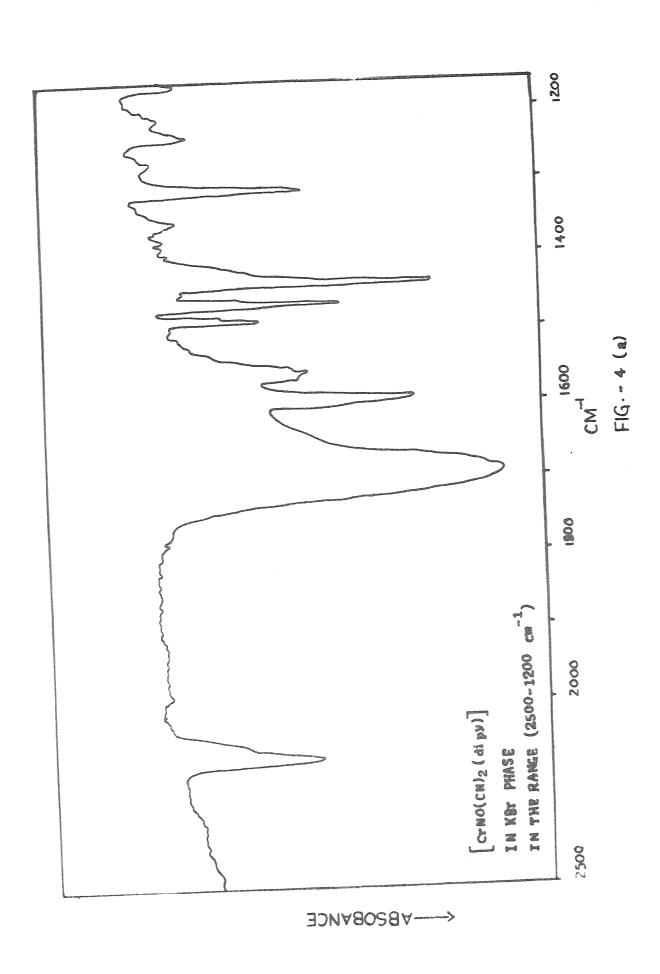
Importent I.R. Spectral bends and assignments

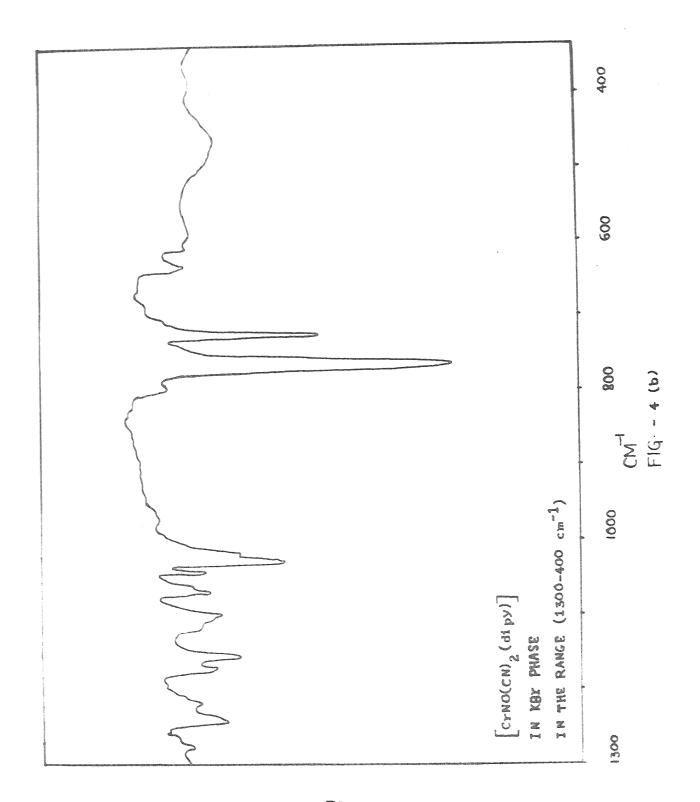
Compound (NCO)		(E)	Organic	Organic ligands	Or anic ligands		Marie S(Como)	
[Criff(Cif), (o-phen)]	1696vs	2156s,	1600s,	1520w,	1500w,	1600s, 1520w, 1500w, 1470m, 625w	625%	392%
N		2125 sh	1425s, 1225v, 7040v,	1370w, 1022m, 650m,	1330 v., 275m, 608v.	1272w, 1060w, 850s,		
[CrNO(CN) <sub>2</sub> (d1py)]	169448	2157s, 2133sh.	14308 14308 10158	13000 10000 7650 8550	122 6 w. 1075 w. 715 w.	1480m, 612 1208w,1175w, 1030w, 480b.	612w 175w,	MO09
[Crito (Cit) 2 (tyy) 2]	1700vs	2125sh.	1600m, 1375w, 1025w,	1530w, 1210m, 1000w,	1450w, 755w,	1076m, 1076m, 695s,	615w	295w
$\left[ \operatorname{crwo}(\operatorname{cm})_{2}(\operatorname{cu})_{2} \right]$	1708vs	2150s,	1600s,	10万0回。	\$ 100 mg	14.15s,	10 30 30	282 E

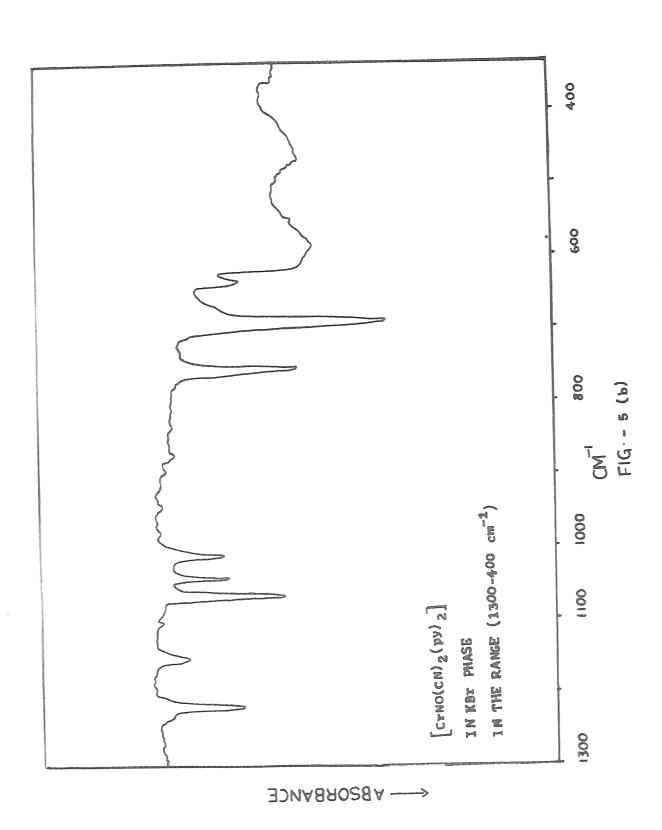
\* Positions ( /cm ) and relative intensities (vs,very strong; s,strong; m,medium; w,weak; b, broad; sh, shoulder). Data taken from flgures. 32,30,48,4b, 5a and 5b.









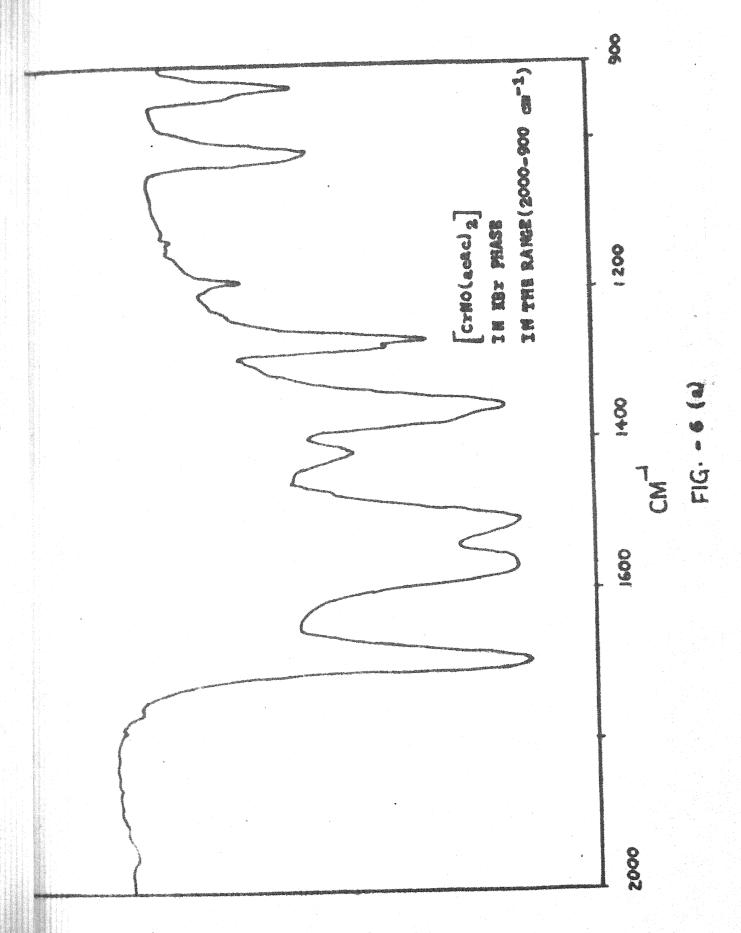


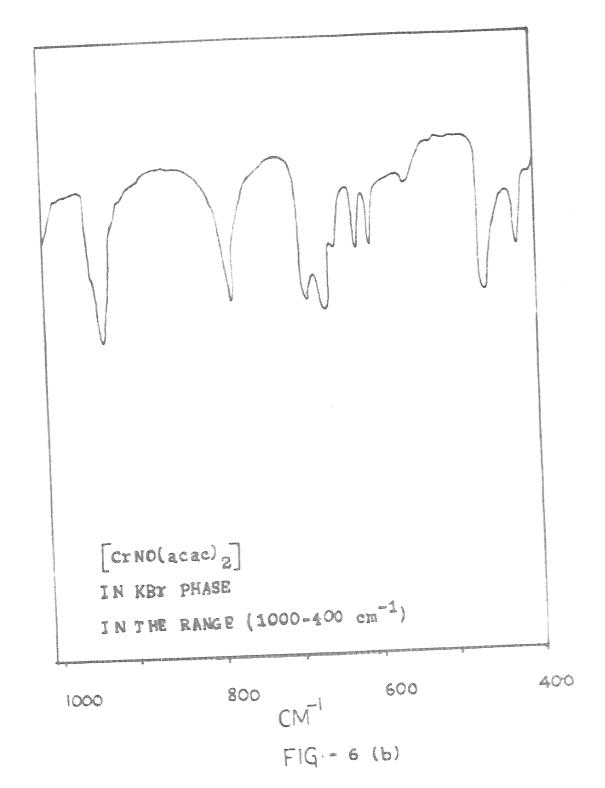
## Teb. 16.

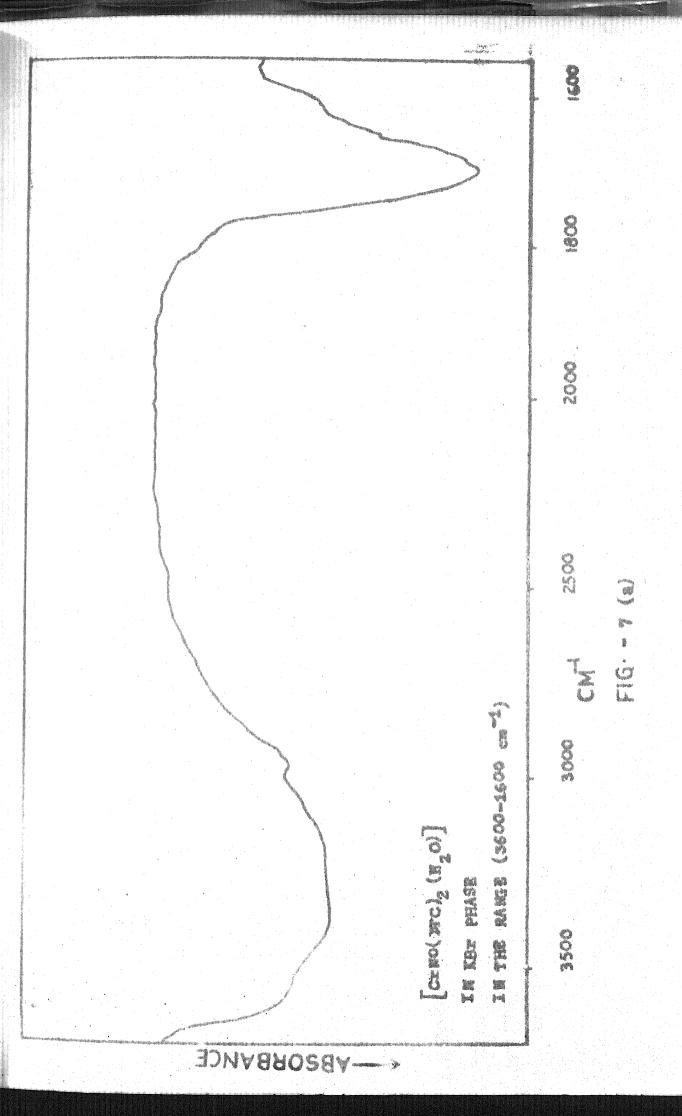
Important I.E. Spectral bands and assignments

	app to the test test test the mile the test tip test to	is high south state while cape with south their tall		dies and deal field deal and			1111	1000
Compound	V(NO)	(HO)(	(H-0-H)9	Organic	Organic Lirands			Organic Ligands McEn of CENO
[Cr(MO) (acac) <sub>2</sub> ] 1692vs		to one of the circ see see see see see see see see see se		1570w, 1360s, 1000m, 780m,	1500w, 1250s, 940m, 695m,	1408w, 1180w, 930m, 676w,	640 <sub>w</sub>	265a
[Crito(dec)2(H20)]	1705vs	3540b,	1620sh	1355w, 1205m, 995w, 780w,	1430m, 1300w, 1145m, 910w,	1375w, 1275m, 1070w, 850w,	620w	27 %

\*Positions( /cm )and relative intensities(vs, very strong; s, strong; m, medium; w. weak; b, broad). Data taken from figures 6a,6b,7a and 7b.







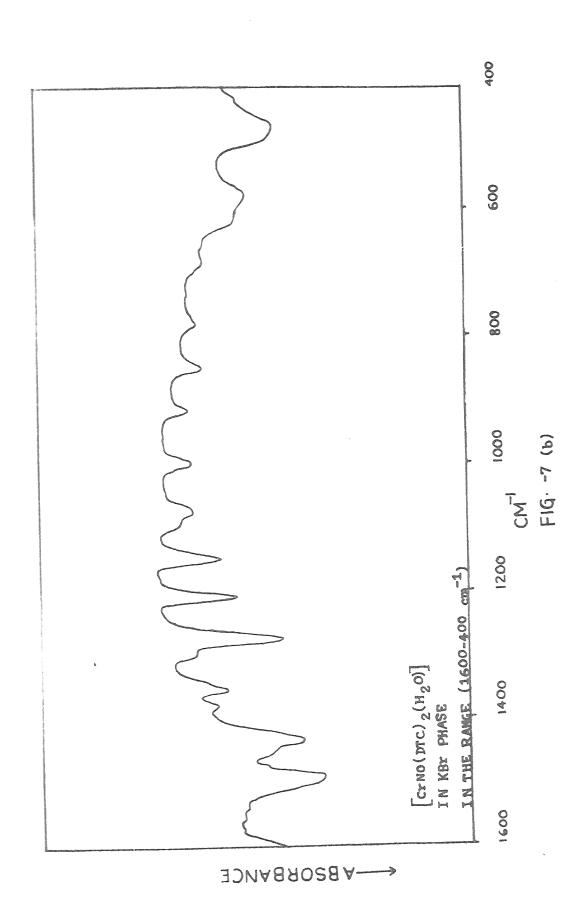
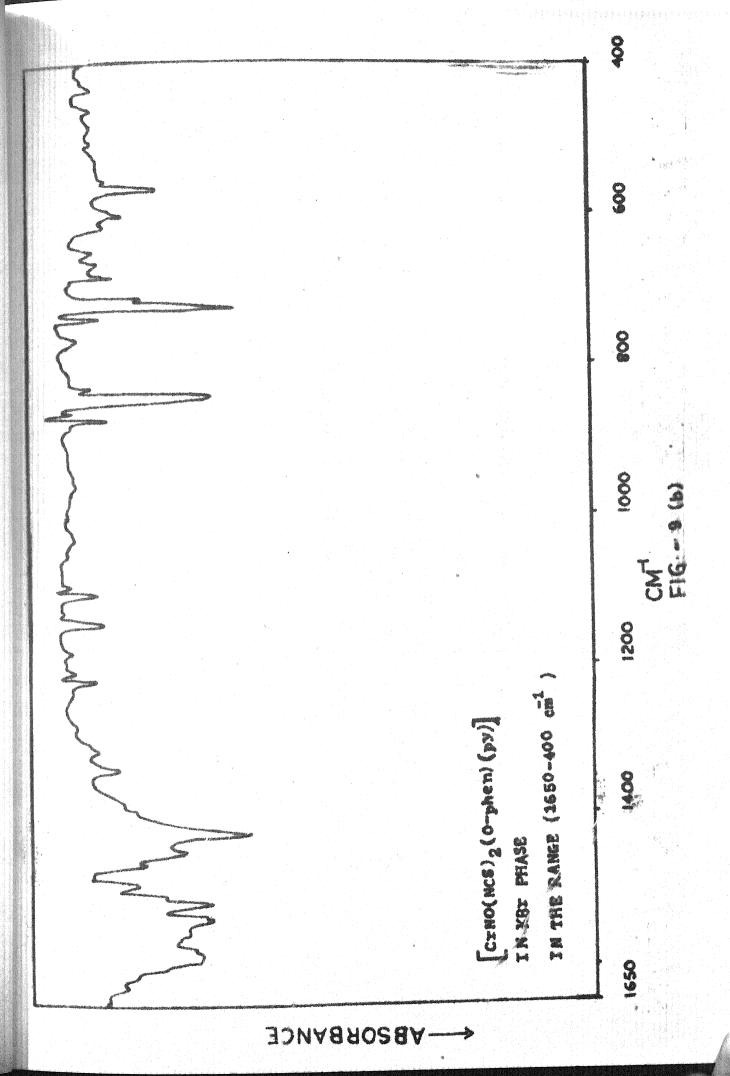


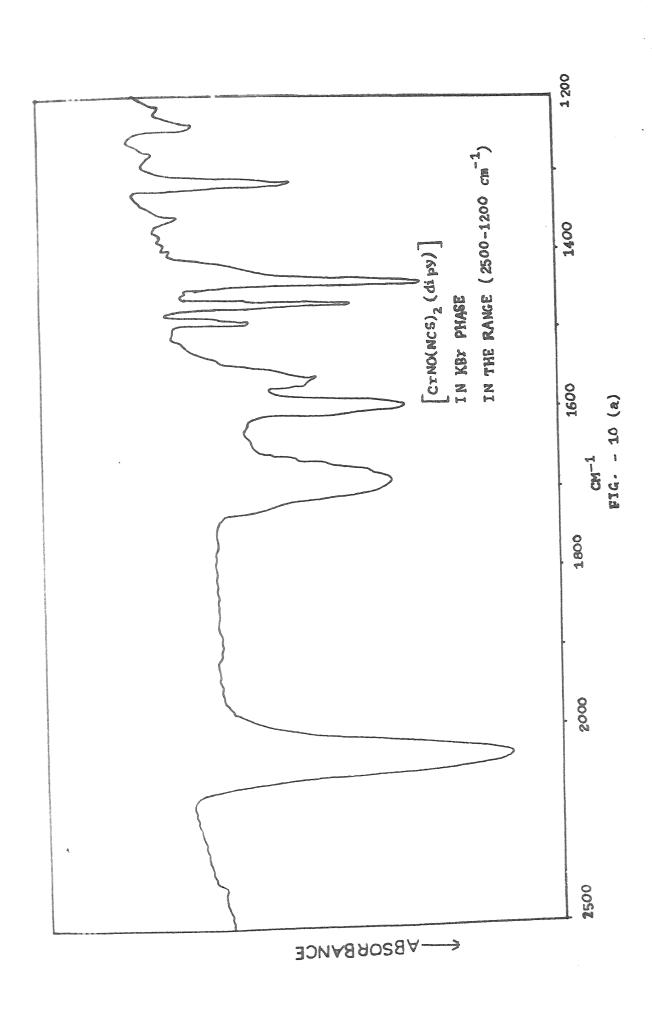
Table-17

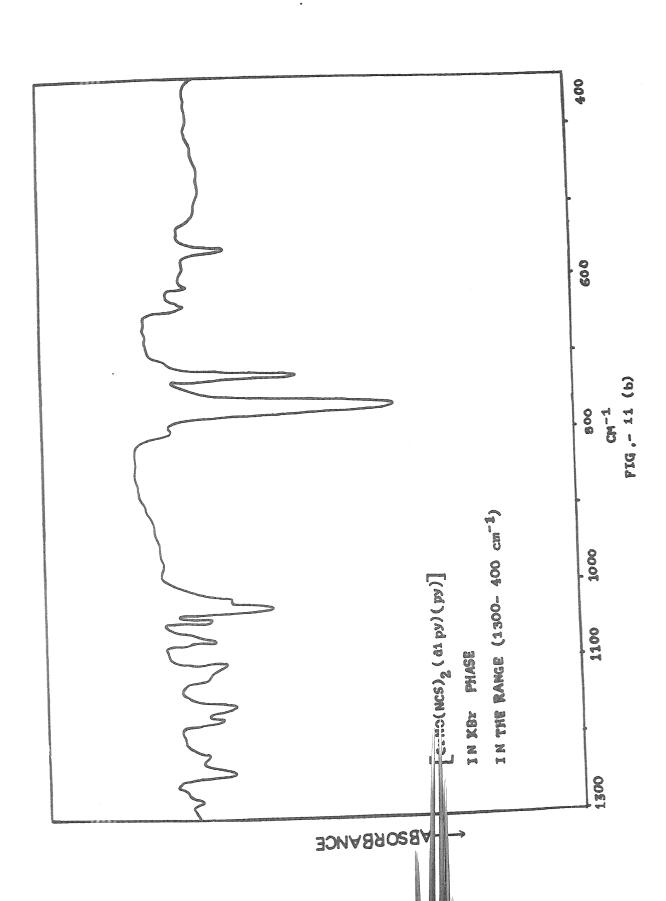
Important I.R. Spectral bands and assignments

	(0)43)(	V(B)		Organic ligands		· 电电子电子电子电子电子电子电子电子电子电子电子电子电子电子电子电子电子电子电	100 eta 100 et0 et0 et0 et0 et0 et	(E.S.)	V(crn) S(crNo)
[CrNO(NCS) <sub>2</sub> (o-phen)]	1710s	2070vs	140w, 1105w, 710m,	1415m, 880w, 685w,	1340w, 845m, 650w.	1220w, 765m,	745w,	W009	565w
[crwo(MCS) <sub>2</sub> (o-phen)(py)] 1710s	1710s	2080vs	1340w 1445w 835w	1535w, 1315w, 770w, 605m,	1515w, 1095w, 7460w,	1451w 210w 725w 446w	1125m, 1180w, 245m,	620m	570w
[Crwo(WCS) <sub>2</sub> (dipy)]	1700s	2070vs	1600m, 1372w, 1165w,	1576w, 1308m, 1150w,	1295w, 1084w, 715m,	1480m, 1250w, 1070w,	1210kg	620w	295w
[crwo(mcs)2(dipy)(py)]	2002 2002	2075vs	1602m, 1310m, 1148w, 800w,	1575w, 1296w, 1088w, 756s,	1050v.	1275m, 1275w, 1020w,	1438v, 1170v, 1014m, 570v.	625w	265m

\* Positions ( /cm 1) and relative intensities (vs, very strong; s, strong; m, medium; w, weak). Data teken from figures 8a, 8b, 9a, 9b, 10a, 10b, 11a and 11b.



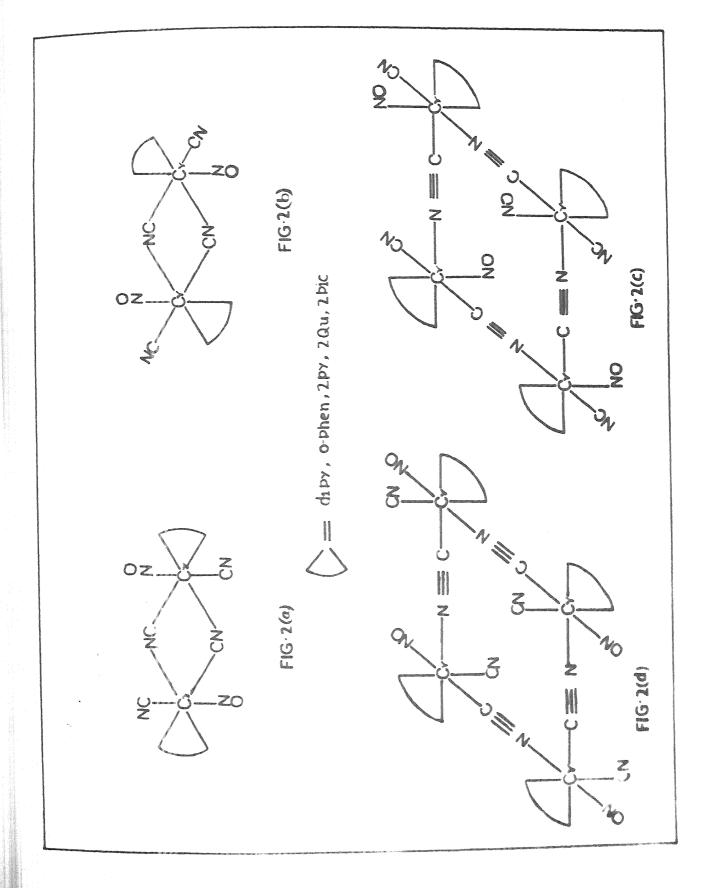




A further possibility of this shift may be due to (a) chance in coordination number (b) the change in the nature of co-ligand in respect to X-bonding capacity. In the series of heterocyclic arcmatic amines and imines derivatives some trend is observed. In the dipyridyl and c-phenanthroline the )(NO) remain almost identical which is slightly lower in frequency to that for the comp exed pyridine or quinoline. This suggests that in the cheleted derivatives metal-nitrogen bond becomes stronger compare to non-chelated darivatives. Though dipyridyl and o-phenanthroline are generally shown to be better T - bonding ligand compare to pyridine or quincline the trend we follow here is abit different. The N-C stretching for the acetylacetoneto complex appears almost identical to that in dipyridyl and c-phenanthroline complexes. This suggests that the N-I stretching remains unaffected with the change of donor atoms of the Ligand used. This is in accordance with the proposition made by Enemark and Feltham. The electronic effect of the metal ion and the coordinated NO group should not be treated as separable entity rather the (CrNO) group can be treated as inorganic functional group". 51 However the position of appearance of )(1.0) in these complexes can be treated in the light of the parent complex as the terminal bonded

containing the linear Cr-NC group, thus ruled out the possibility of nitrosyl group to act as brindging group. Hence the polymeric nature of the cyano substituted complexes as supported by their generalinsolubility in different common solvents, their resistivity in alkyltion reaction (vide experimental section) and their unusual low magnetic moment values along with broadening in e.s.r. spectra (vide infra) can be accounted for by presuming a cyano bridged structure as shown in fig. 2a, 2b. 2c and 2d. Solid state spectra of all these derivatives show two cyanide stretchings appearing in identical positions that is at 2150-2157 and at 2125-2133 cm . The lower band aplears as shoulder in all the cases. In bridged cyano complexes, the bridging is encountered only in the form of  $N-C \equiv N-C^{\circ}$ , which results V(CN)to shift to a higher frequency  $^{42}$ . We assign the  $\mathcal{V}(CN)$ at 2150-2157 cm 1 for the bridging cyano groups and the rest one for each complex for the terminal cyano groups (fig.2). However four possibilities exist for the bridge structure (fig. 2a, 2b, 2c and 2d). Fig. 2a and 2b represent a dimeric structure satisfying a hexacoordination of the central metal using cyano bridged structure. Fig. 2c and 2d represent a tetrametic structure leading to hexacoordinated structure of the central metal with cyanide bridge. The dimeric structure is

di.



unfavourable in the sense that here a linear arrangement of the cyano bridge moiety is not possible. The other reported cyano bridge complexes contain only the linear attachemtn P-C=N-P. 42. Recently Bustin 118 through electrochemical studies on the reaction of [Cr(CN)(H20) NO] + with Ag and Hg 2+ ions proposed that the bridge structure like Cr-N-C-M(M/=Ag\*, Hg2+) is formed. The CN bridged linkage isomer like Cr-C-N-N (N=Hg2+) has also been characterised. Thus in accordance with the linear cyano bridge structure, the tetrameric structures ( fig. 2c and 2d) are favourable. It has been shown by Raynor and coworkers 115 that in acid hydrolysis of pentacyanonitrosylchromate(I) anion, the first aquation takes place to the cyanide group in exial position that is trans to the nitrosyl group. Taking into account of this trans directing effect of the nitrosyl in the tetrameric structures, the structure, 2d is untenable. Hence all these evidences are in conformity with the structure, 2c.

In aquo bis (diethyldithiccarbanato)nitrosyl(I) chromium(I), a slightly higher )(NO)compage to that of bis(acetylacetonato)nitrosylchromium(I)(Table-16) is in conformity to the e.s.r. result (vide infra). It is known that lower coordination number, higher the observed frequencies and the reverse trend observed as described in the preceeding lines further support that

dithiocarbamate is a better complexing ligand than the acetylacetonate.

In the thiocyanato substituted complexes the infrared spectral bands and their tentative assignments are presented in Table-17. The thiocyanate group may coordinate to the metal through either the nitrogen or the sulphur atom or both. Chromium being in the first transitional series, has been placed as class A metal 119. On coordination the V(CN) frequency of NCS" is lowered in N-bonded complexes than in the 5-bonded complexes 120. A comparison of the observed cvanide stretching with those of the known thiocyanato complexes 42 suggest N-bonded thiocyanate group in these complexes. The use of )(CS) to say more about the nature of coordination could not be possible here because of the presence of several other bands originated from the organic ligands in this region. However, the greater complexity in the e.s.r. spectra of these complexes(vide infra) suggests the coordination through nitrogen.

A comparison with the corresponding substituted cyano complexes, for example, [CrNO(CN)2(o-phen)] with [CrNO(NCS)2(o-phen)] is highly interesting. The former is proposed to be polymeric in nature whereas the latter is a monomer. This difference may be attributed due to the lack of chromium to coordinate through

sulphur of the thiocyanato group. This is expected regarding the classification of chromium as a class A<sup>119</sup> metal.

### D(CrNB) and 8(Cr-N-D) vibration :-

As discaussed in the introduction (vide supra), the complete assignment of these vibrations require isotope substitution data supplemented by Raman Spectra. For nitrosyl complexes the complete agreement of the vibrational spectra through analyses has been achieved only with  $\{RuNO\}^6$  complexes  $^{121-127}$ . The controversy on the assignment of these vibrations have been settled, the  $\Sigma(RuNO)$  be assigned to a band around 600 cm  $^{-1}$  and  $\Sigma(Ru-N-O)$  has been assigned at some what lower frequency, though sub-reversal of the assignments are reported  $^{123}$ .

Among the complexes described here the bis (acetylacetonato) nitrosylchromium (I) shows somewhat clear spectrum (fig.14). In the range 700-385 cm<sup>-1</sup> a few sharp bands are observed in acetylacetonato complex which are consisted mainly in three band envelopes. The first envelope contains sharp bands at 675,654, 640 cm<sup>-1</sup>, the second at 610 and 592 cm<sup>-1</sup> and the third one at 454 and 412 cm<sup>-1</sup> respectively. The nature of the first and third envelopes are identical to that observed by Mikami and coworkers 128 for several square planar acetylacetanato complexes of bivalent metals.

The bands in second envelope then should be due to Cr-N streaching and Cr-N-0 bending vibrations respectively as reported by Miki<sup>40</sup>. For complexes containing nitrogen donors and dithiocarbamato complex, the appearance of bands at similar wave numbers could not be assigned with certainty as these aromatic bases and dithiocarbamate have their vibrations which appear at similar wave numbers, thus complicating these assignments. However, tentative assignments can be made for bands appeared in the range 585-596 cm<sup>-1</sup> and 624-612 cm<sup>-1</sup> for Cr-N-0 bending and Cr-N stretching vibrations for these complexes.

### Organic ligands vibrations :-

That the organic molecules in the complexes are coordinated to chromium is indicated by shifts in the ligand bands in the spectra of the complexes from their positions in the spectra of the free ligands. Similar shifts on complexation have been characterised in several metal complexes using these ligands. 42,129,130 Electron spin resonance Spectra:

The e.s.r. data of the synthesised complexes are presented in Table-19. The reported values for the earlier known complexes are also set out in Table-16. The monomeric bis (acetylacetonato) nitrosylchromium (I) shows some interesting features. Its spectra as powdered sample and diluted in KBr (fig. 12a) show a tetragonal distortion

Table-18

Electron spin resonance parameters for known(CrNU)<sup>2+</sup>

complexes.

	THE REST COME SHAPE WHEN SHAPE SHAPE SHAPE SHAPE AND ADDRESS.		Company of the compan
Complex	g(av)	A(n),G	Reference
Trans- [CrNO(C1) (diars) <sub>2</sub> ] ClO <sub>4</sub>	2.00	e trans construction graph scale and a re- construction graph code code construction graph code code code code code code code code	The state when the state was done and the state when the state whe
[ cxN0 (CN) 5] -3	1.99	5.3	132
[C#NO (NH3)5]2+	1.98	6.98	133
[c=N0 (H20) 5]2+	1.97	5.4	133
[cxN0(CNS)5]3-	1.970	quina	26

Table-19.

Electron spin resonance parameters for (CrNO)<sup>2+</sup>

complexes

Complex	g (av)	A(n),G
[CrNO(CN) <sub>2</sub> (o-phen)] undiluted in powder form	1.980	
[CrNU (acac)2] in ethanol	1.987	5.6
CrNO(acac) in ethanol with pyridine	1.990	
[CrNO(acac),]	1.970	
	= 1.990	
911	= 1.951	
Undiluted in powder form	1.980	
[CrN0 (DTC) 2 (H20)] undiluted in powder form	1.990	
[GrNG(NCS) <sub>2</sub> (o-phen)] undiluted in powder form	1.970	
[CrNC(NCS) <sub>2</sub> (o-phen)(py)]	1.978	
undiluted in powder form		

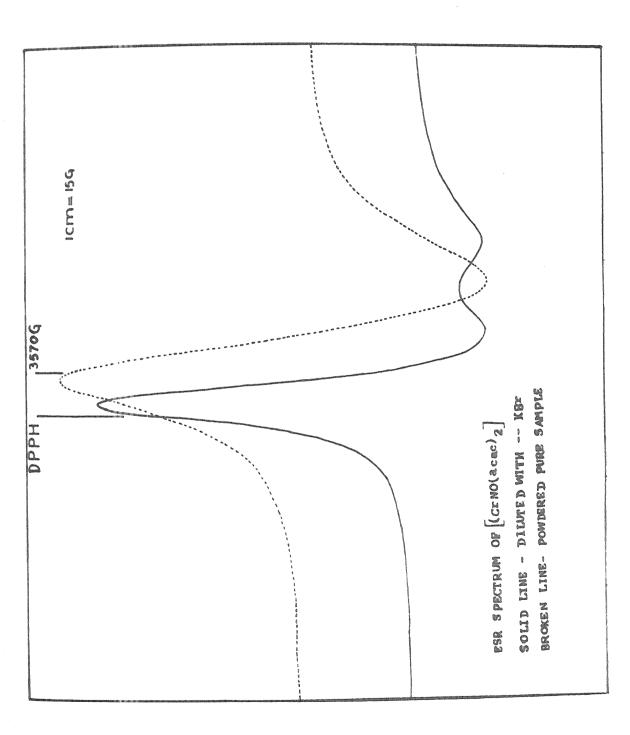


FIG. - 12 (a)

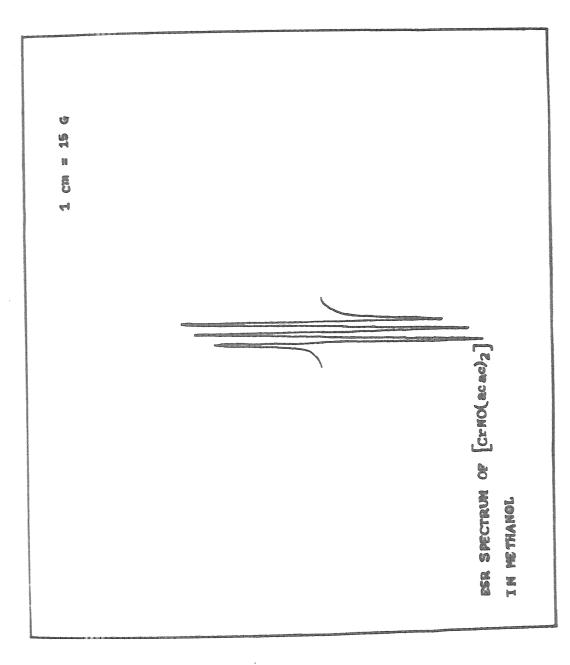
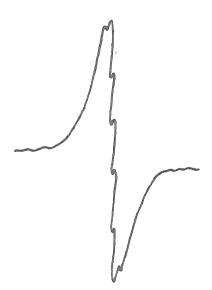


FIG .- 12 (b)

1 cm = 15 G



ESR SPECTRUM OF [CrNO(acac)<sub>2</sub>]
IN PYRIDINE - METHANOL

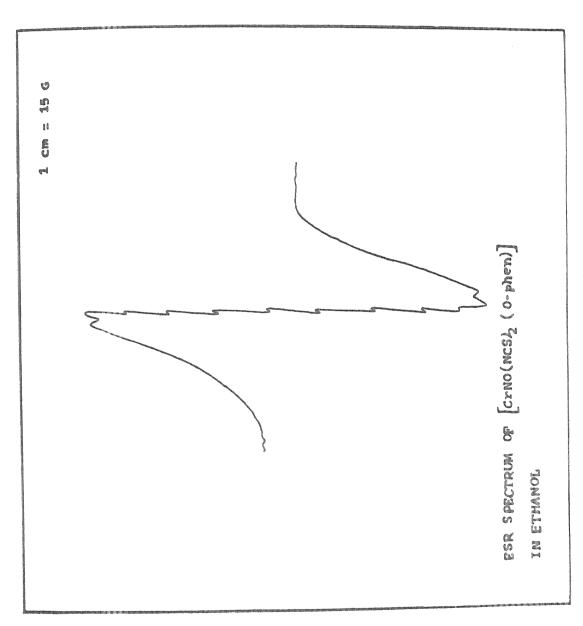


FIG. - 13

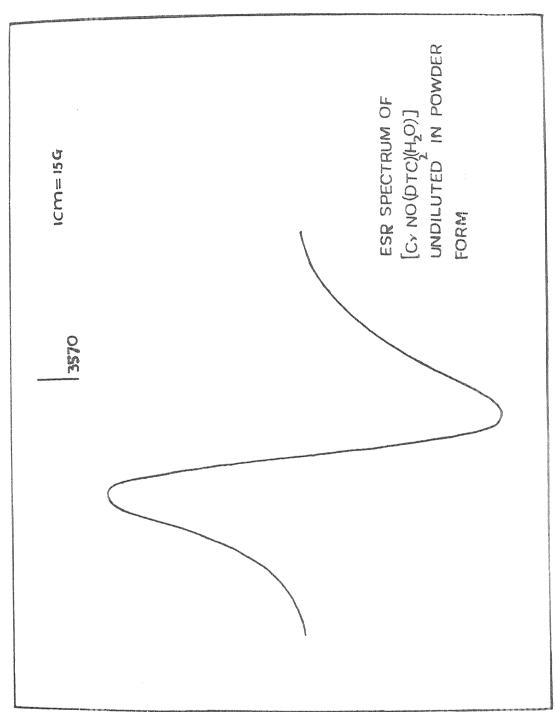
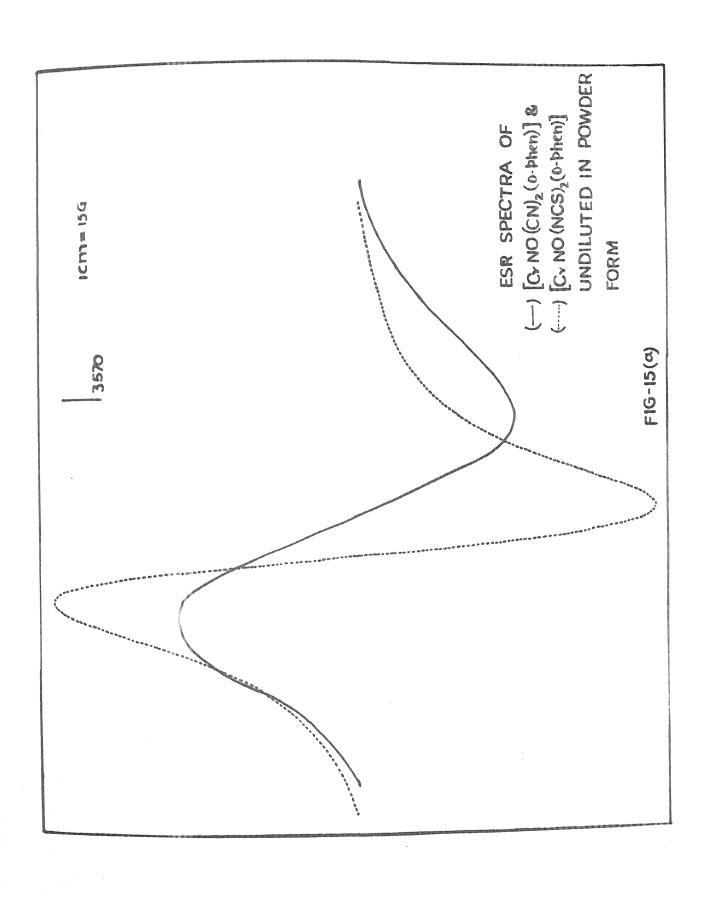
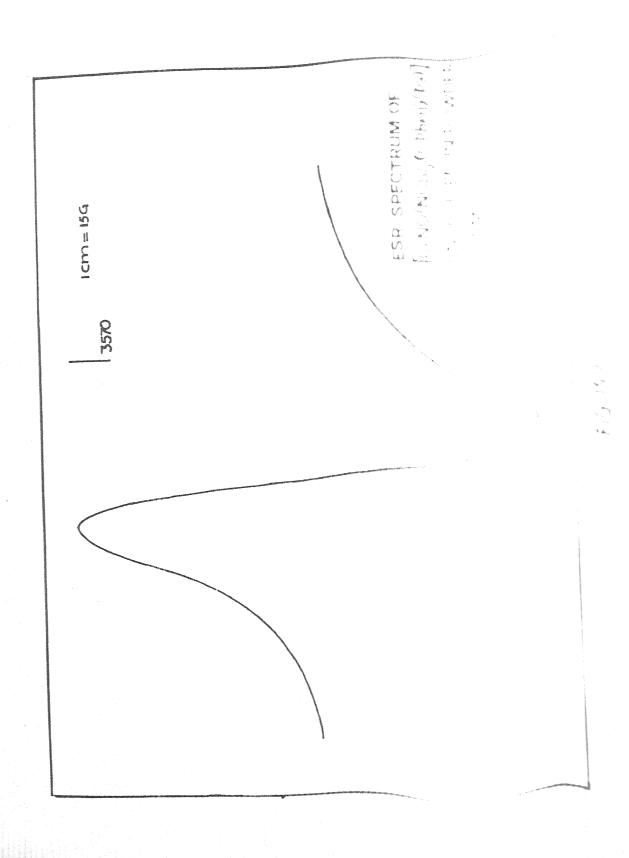


FIG.14





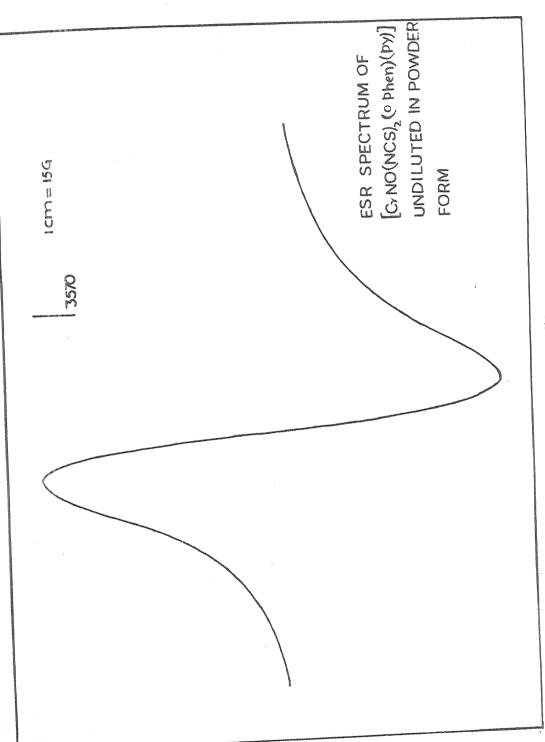


FIG-15(b)

in the complex. The value of g(ag) obtained from g and g is in very good agreement with the 'g' value obtained from undiluted spectra. A comparison of the g(iso) and the nuclear splitting of the nitrogen, A(n) of the complexes so far known suggest the delocalisation ability of the various ligands attached to (CrNO)<sup>2+</sup> group as follows:

diars >  $CN^-$  > acac >  $NH_3$  >  $SCN^-$  >  $H_20$  . However the 'g' value obtained from the solution spectrum of acetylacetonato complex shows abit higher value than that obtained from the solid spectra. This suggests that in solution the complex may be solvated in the axial position trans to No. As ethanol is used as a solvent the interaction with the oxygen atom which has got no nuclear spin does not produce any superhyperfine splitting (fig. 12b). As a test a spectrum in ethanol treated with slight pyridine is under taken. Fig. 12c shows that the interaction of the pyridine's nitrogen (I=1) takes place with the well resolved three lines spectrum of the complex in ethanol. The 14N nucleus of pyridine interact sausing a complex spectrum which would not be resolved further. However, the 'g' value and the complexity of the spectrum are suggestive enough to say that the pyridine is coordinated at the sixth

site according to the following reaction.

[CrNO(acac)2] +py ---> [CrNO(acac)2 (py)]

The corresponding dithiocarbamato complex as such has been isolated as hexacoordinated species. A comparison of the 'g' value (fig. 14) with others suggests that its delocalisation ability falls in between cyanide and actylecetonate ligands.

The substituted cyanonitrosyl complexes are highly insoluble in nature and only the powdered spectra are taken which revealed nothing important to throw light for their lower magnetic moment values or about polymeric nature. However, a comparison of the cyano derivatives along with the thio-cyanatoderivatives resulted one interesting observation. The powdered spectra of [CrNO(CN)2(o-phen)] and [CrNG(NCS)2(o-phen)] presented in fig. 15a suggest that the line width (between point of maximum slope) of the cyano substituted complex is greater (93.0 gauss) then that of the thiocyanato substituted complex (42.0 gauss). Taking into consideration of the metal complexing ability of cyanide than thiocyanato group and the change in mass between these complexes by the units of two sulphur atoms, the broadening of the spectrum of the former complex may be attributed due to exchange broadening caused by interaction due

to polymeric state of the complex.

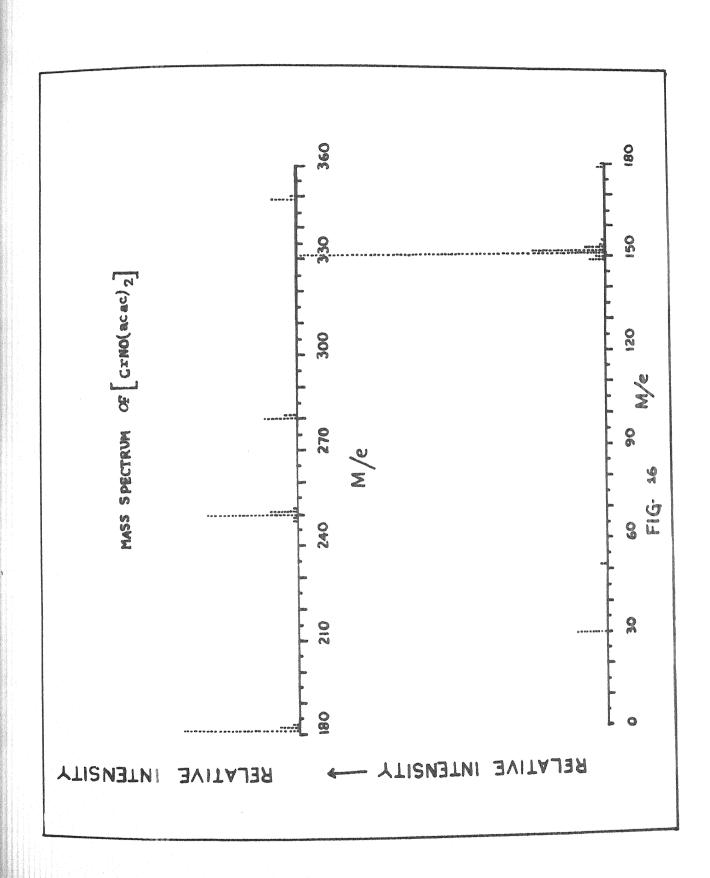
The athanolic solution spectrum of [CrNO(NCS)<sub>2</sub> (o-phen)] (fig.13) consists of a broad line and the line shape shows the interaction of the superhyperfine splitting due to <sup>14</sup>N of No is masked by further hyperfine splitting from the <sup>14</sup>N nuclei of the two nitrogens of phenanthroline ligand along with those of the thiocyanate groups.

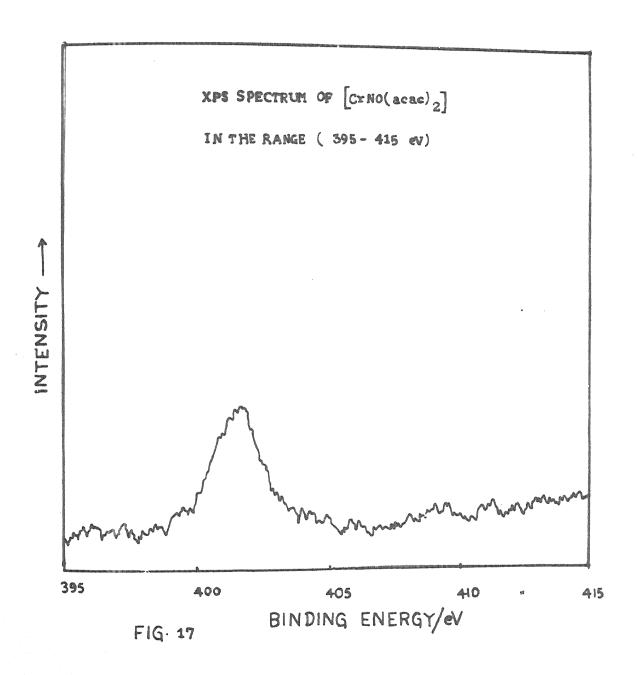
## Mass spectra :-

The mass spectrum of [CrN0(acac)<sub>2</sub>] is presented in fig.16. Besides the appearence of parent ion peak at 280(M/e), ions like  $\text{N6}^+$ ,  $\text{Cr}^+$ ,  $\text{CrN0}(\text{acac})^+$ ,  $\text{Cr}(\text{acac})^+_2$  and  $\text{Cr}(\text{acac})^+_3$  are observed. The observation of each peak are in accordance with the different exidation states of chromium. The most intense peak is observed for  $\text{Cr}(\text{acac})^+_2$ . However, the molecular ion peak is of low intensity which is comparable to that observed in even for  $\text{Cr}(\text{acac})^+_3$ . However, the monomeric nature of the complex is here established.

## X-rey photoelectron spectroscopy :-

The Xps spectrum of  $[CrNE(acac)_2]$  in the binding energy range 395-415 eV is presented in fig. 17. The N(1s) value 401.8 eV is comparable to that reported for the  $K_3[CrNO(CN)_5]^{55}$ . The slight increase may be accounted for the neutral nature of the complex





compared to parent cyanonitrosylchromium(I)anion. The slight increase of this value also tallies with the increase of (NO) in its infrared spectrum (vide Supra). The observed axial symmetry of the 'g' tensor for this complex as discussed earlier is also in accord to the presence of linear Cr-N-O Group.

## Electronic Spectra :-

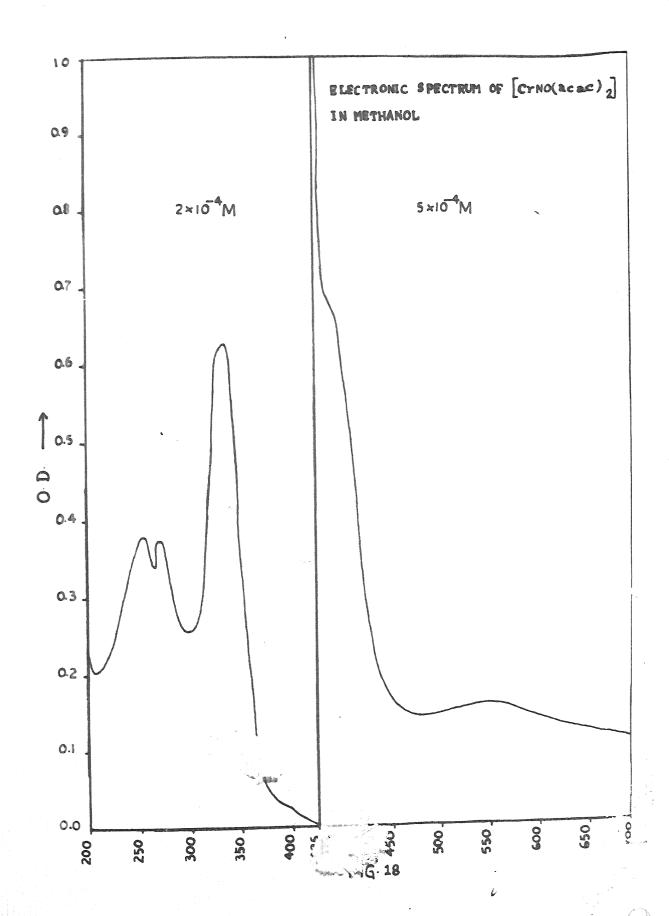
Reflectance spectra of the powdered solid complexes, [CxN0(CN), L, L, dipy, o-phen, 2 Qu, 2py ) and [CrN0 (acac) and solution spectrum of the acetylacetonato complex are recorded in the range 200-750 nm. Peak positions are presented in Table-20, where for comparison, peak positions of the parent compound and of some alike compounds as taken by Griffith 23 are also included. The important feature of these electronic spectra is that these complexes whow four well resolved peaks, which are numbered for convenience of reference as in Table-20. The 3rd peak deserves special comments. For the isolated complexes in this investigation, it is the most intense peak among all the four peaks observed. The discussion would be restricted here on dipyridyl substituted complex taking it as representative of this class of compound along with the acetylacetonato complex. For free dipyridyl the first peak which appears at 280.1 nm., correspends essentially to  $x=-\frac{\pi}{x}$  transition. Coordination of

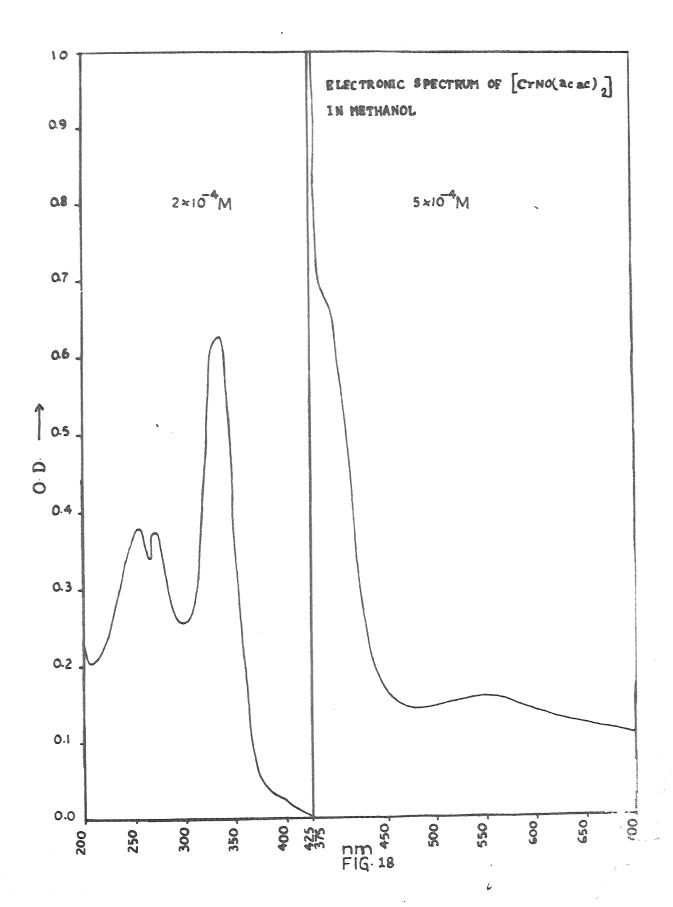
## Teble-20.

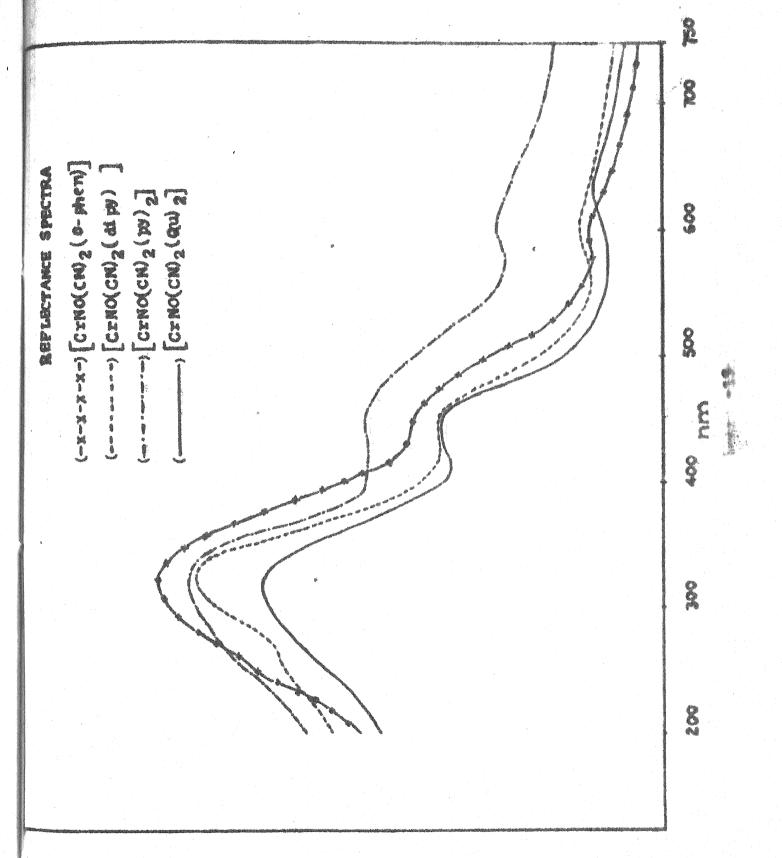
# Meetronic spectra

		2nd		4th	Ref.
Gello (ca) 2 (dipy)	295.2	450.0	25.9	24.9	
[crito(crit)2(o-phen)]	591.0	450.0	325.7	246.1	
[Carifo (car) 2 (qu) 2]	635.9	9.644	327.8	248.7	
[crito(cr)2(py)2]	598.0	150.0	327.3	252.8	
[crito(acae) 2]	550.0	394.0	337.4	261.9	
[Crifo(acac)2]in Methanol	550.0(32)	394.0(135)	337.2(3120)	270.0(1860)	
N <sub>3</sub> [CrNO (CN) <sub>5</sub> ] in aqueous solution.	724.0(14.5)	447.0(127)	335.0(86)	270.0(2448)	238
[Grifo(H20)5](Glo <sub>4</sub> )2 in aqueous solution.	567.0(30.6)	447.0(131)	390.0(96)	324.0(101)	200
[Crwo(MR3)5] C. in aqueous solution.	457.0(101)	348.0(69)	302.0(157)	257.0(1160)	238

<sup>\*</sup> Peak positions in nm and for solution spectra, extinction coefficients, , ( /mole cm )in parentheses. Deta taken from figs. 18,19 and published results.







this with metal ion results in a red shift with the often splitting of this peak 135. In identical nitrosylcyano complex of iron(II) 136 this red shift followed by splitting is clearly observed and the position of the appearance of this peak suggests that the X-system of the dipyridyl does not affect much the X-system of NO by comparing the peak positions of nitroprusside anion 43, 137 with that of the dipyridyl substituted cyanonitrosyl of iron(II) 136. The 3rd peak observed at 335.0 nm in pentacyanonitrosylchromate(I)anion is less intense than the 2nd peak, obviously it can not mask thex- x transition of coordinated dipyridyl. Thus the 3rd peak at 325.2 nm is mainly responsible for  $x = \frac{*}{\pi}$  transition of complexed dipyridyl. The appreciable red shift of this band which has no parallel in other dipyridyl complexes, 135, 136 suggests the considerable mixing between the T - systems of dipyridyl and (CrNC) modety in these complexes. The acetylacetonato complex also gives evidence of the considerable red shift of its  $\pi$  -  $\pi$  transition that is from 290.8 nm to 337.2 nm which also supports this view. From the intensity of the 4th peak in all these complexes along with the nature of the extinction coefficient of the acetylacetonato complex, it may be presumed that this peak for all these complexes can also be assigned to strong  $X = \frac{*}{\pi}$  transition of the complexed ligand moiety 139,140

For peaks 1st and 2nd, the low intensity nature of these peaks in all these complexes followed by extinction coefficients of such peaks of acetylacetonato complex suggest them predominatly of 'd-d' type transitions.

Unlike the e.s.r. spectrum (vide supra), the solution (methanol) electronic spectrum of bis (acety-lacetonato) nitrosylchromium(I) does not give any clue of the solvation at the sixth position trans to NO as the solid state and solution electronic spectra of this compound give absorption peaks at indentical postitons.

## Chapter IV

### SUMMARY.

The thesis comprising the results of the investigations on the nitrosyl complexes of monovalent chromium, has been divided into three chapters.

In chapter I, a brief and general account of the cyanonitrosyl complexes has been given. The use of different physico-chemical methods in elucidating the bonding nature and structural aspects of these complexes are also reviewed. Based on these, a broad account of the chemistry of nitrosyl chromium(I) complexes has been given. From the synthetic point of view, the derivatives, the knowledge about which are only exist in solution studies, are synthesized. As an autcome of these, the scope of the present work has been stressed.

Chapter II describes the materials and methods involved in the present work in details which has been subdivided into two main parts. Chapter II—A describes the analytical methods used for the characterisation of the newly prepared complexes. Chapter II—B describes the preparation and proparties of the newly synthesized compounds. As this type of substitution reactions have got no parallel among other nitrosyl cyano complexes of transition metals except ruthenium and to some extent iron, some analogies were tried to establish. Based on the substituent groups of these mixed ligand nitrosyl

cyano complexes of chromium(I), chapter II-B was further divided into four sub-headings. Chapter II-B.1 describes the preparation and properties of a series of nitrosyl chromium complexes having general formula  $[CrNO(CN)_2L_2]$  (where  $L_2$ =0-phen, dipy, 2 Qu, 2 py, 2 picoline)starting from the sobstitution reaction of  $K_3[CrNO(CN)_5]$ . $H_2O$  with these nitrogen donors. The reaction can be generalised as below.

The remarkable chemical dissimilarties of these complexes with those of other metals nitrosylcyano derivatives were shown by comparison. Chemical inertness of cyano groups present in the representative complex,

[CrNG(CN)<sub>2</sub>(dipy)] of this class has been shown by failure of the reaction of the following types:

[CrNG(CN)<sub>2</sub>(dipy)] + excess dipy sealed tube no change.

[CrNG(CN)<sub>2</sub>(dipy)] + CH<sub>3</sub>I sealed tube no change.

[CrNG(CN)<sub>2</sub>(dipy)] + CH<sub>3</sub>I sealed tube partial decomposition with no change.

Chapter II-B.2 and B.3 describe the preparation and properties of bis(acetylacetonate)nitrosylchromium(I), [CrN0 (acac)<sub>2</sub>] and aquobis (diethyldithiocarbamato)nitrosylchromium(I), [CrN0 (DTC)<sub>2</sub> (H<sub>2</sub>0)]. Interestingly the corresponding dithiocarbamato complex can be isolated as

hexacoordinated species whereas the corresponding acetylacetonato complex is pentacoordinated. In solution the acetylacetonato complex remains solvated as  $[CrNO(acac)_2S]$  (where S = donor solvent molecule). This has been particularly demonstrated in ethanol solution using traces of pyridine and the enteraction has been followed spectroscopically (vide supra).

Chapter II-B.4 discribes the preparation and properties of the thiocyanato substituted complexes of the general formulae CrNU(NCS)2L2 (L2= dipy and o-phen) and [CrNU(NCS)2L2(py)]. All these complexes are found to be nonelectrolytic in nature.

Chapter III describes the physicochemical investigations of the isolated complexes. The studies include
magnetic susceptibility, infrared, electron spin resonance,
mass, X-ray photoelectron and electronic spectral measurements.

The magnetic moment values of the prepared complexes after correction for diamagnetic contributions of the ligends are in the range from 1.60 B.M. to 1.74 B.M. These values are consistent with a low spin d<sup>5</sup> configuration. This is in expectation as the ligands involved in the preparation of the complexes are mostly x- bonding type and hence should be of low spin type containing one unpaired electron. The slightly higher magnetic moment

(1.87 B.M.) for the parent complex,  $K_3$  [CrN0 (CN) 5].H20 is due to spin and orbital interaction in the complex. It is remarkable to note that the magnetic moment values (1.60-1.66 B.M.) of the cyano substituted complexes are lower than acetylacetonato complex. On the other hand the magnetic moment values of thiocyanato nitrosyl complexes are close to spin only formula. This suggests the polymeric nature of the cyanonitrosyl complexes and monomeric nature of the acetylacetonato and thiocyanato derivatives.

Characteristic stretching frequencies of different coordinating ligands have been assigned in the infrared spectral studies. The  $\Im(\mathrm{Nu})$  of the isolated complexes is in the range  $1694\text{-}1710~\mathrm{cm}^{-1}$  which is comparable to the  $\Im(\mathrm{Nu})$  of the known complexes. Solid state spectra of all the cyanosubstituted complexes give two cyanide stretchings in identical positions that is at 2150-2156 and at  $2125\text{-}2133~\mathrm{cm}^{-1}$ . The lower band appears as shoulder in all these complexes. The  $\Im(\mathrm{CN})$  at  $2150~\mathrm{cm}^{-1}$  is assigned for the bridging cyano groups and the rest one for each complexes for the terminal cyano group. Various probable structures have been assigned for these complexes. The structure, fig.2c, is finally said to be correct among them. This

and valuable results of K. Nakamoto. 42

The  $\Im(NO)$  in aquobis(diethyldithiocarbamato)nitrosylchromium(I) is slightly higher than in acetylacetonato
derivative and the dithiocarbamate is assigned as better
complexing ligand than acetylacetonate.

In thiocyanato substituted complexes, the bonding of chromium through 'N' of the thiocyanato group is suggested by comparing the observed cyanide stretching in these complexes with those of the known thiocyanato complexes. These complexes are assigned to be monomeric in nature due to lack of chromium to coordinate through 'S' of the thiocyanato group.

The  $\Im(\text{CrNL})$  and  $\Im(\text{Cr-N-U})$  have been assigned in the range 600-625 cm<sup>-1</sup> and 595-600 cm<sup>-1</sup> respectively for all the prepared complexes in this investigation.

made for some of the prepared complexes. Tetragonal distortion in all these complexes is clearly reflected through the shape of the spectrum. The solvation in bis (acetylacetonato)nitrosylchromium(I) at the sixth position trans to NO is suggested through this study. The e.s.r. spectrum of this complex in ethanol treated with traces of pyridine shows the interaction of the pyridine's nitrogen(I = 1) with the well resolved three lines spectrum of the complex. The 'g' value and the complexity of the spectrum suggest that the pyridine is coordinated at the sixth

mate complex is compared with other complexes which indicates that the delocalisation ability of this ligand is in between cyanide and acetylacetenate ligand.

The e.s.r. spectra of the undiluted powdered samples of [CrNU(CN)2(o-phen)] and [CrNU(NCS)2(o-phen)] clearly indicate that the line width of the cyanosubstituted complexes is greater than that of the thiocyanato substituted complex. This broadening of the spectrum of cyanosubstituted complexes may be presumed due to exchange broadening caused by interaction due to polymeric nature of the complex.

The only well established compound [CrNO(acac)<sub>2</sub>] containing exygen as donor atoms of other co-ligands has sharp melting point and hence subjected to mass spectral studies. The observation of each peak in this spectrum are in accordance with the different exidation states of chromium. The monomeric nature of the complex is suggested through this study.

The X-ray photoelectron spectral studies is only made for bis(acetylacetonate)nitrosylchromium(I) complex due to the reason mentioned in above para. Other complexes contain nitrogen donor which may affect the N(1s) binding energy of the NO group and hence could not be subjected to this study. The N(1s) binding energy value 401.8 eV

for this complex is comparable to the parent complex, K3 [CrNO(CN)5]H20.

The reflectance spectra of some of the cyanosubstituted complexes,  $[CrNU(CN)_2L_2](L_2=c-phen, dipy, 2py, 2qu)$  and electronic spectrum ofbis(acetylacetonato)nitrosylchromium(I) in methanol are described. All these complexes show four well resolved peaks which are comparable to these reported for the parent complex,  $K_3[CrNU(CN)_5]^{H_2}$ .

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